

David M. Himmelblau / James B. Riggs

Basic Principles and Calculations in Chemical Engineering

Seventh Edition

Prentice Hall International Series
in the Physical and Chemical
Engineering Sciences



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SEVENTH EDITION

BASIC PRINCIPLES AND CALCULATIONS IN CHEMICAL ENGINEERING

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To Betty for the 7th time

DMH

To Brenda, Michelle, J. Michael, and Matt

JBR

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PH PTR acknowledges its auspicious beginnings while it looks to the future for inspiration. We continue to evolve and break new ground in publishing by providing today's professionals with tomorrow's solutions.



CONTENTS

PREFACE	xv
READ ME	xxi
FREQUENTLY ASKED QUESTIONS	xxv

PART 1 INTRODUCTION	1
1 DIMENSIONS, UNITS, AND THEIR CONVERSION	5
1.1 Units and Dimensions	6
1.2 Operations with Units	11
1.3 Conversion of Units and Conversion Factors	14
1.4 Dimensional Consistency (Homogeneity)	21
1.5 Significant Figures	24
1.6 Validation of Problem Solutions	30
2 MOLES, DENSITY, AND CONCENTRATION	43
2.1 The Mole	43
2.2 Density	48

2.3	Specific Gravity	51
2.4	Flow Rate	56
2.5	Mole Fraction and Mass (Weight) Fraction	57
2.6	Analyses of Multicomponent Solutions and Mixtures	59
2.7	Concentration	62
3	CHOOSING A BASIS	78
4	TEMPERATURE	89
5	PRESSURE	99
5.1	Pressure and Its Units	100
5.2	Measurement of Pressure	103
5.3	Differential Pressure Measurements	114
PART 2	MATERIAL BALANCES	129
6	INTRODUCTION TO MATERIAL BALANCES	133
6.1	The Concept of a Material Balance	134
6.2	Open and Closed Systems	136
6.3	Steady-State and Unsteady-State Systems	138
6.4	Multiple Component Systems	144
6.5	Accounting for Chemical Reactions in Material Balances	149
6.6	Material Balances for Batch and Semi-Batch Processes	151
7	A GENERAL STRATEGY FOR SOLVING MATERIAL BALANCE PROBLEMS	166
7.1	Problem Solving	167
7.2	The Strategy for Solving Problems	168
8	SOLVING MATERIAL BALANCE PROBLEMS FOR SINGLE UNITS WITHOUT REACTION	196

9	THE CHEMICAL REACTION EQUATION AND STOICHIOMETRY	225
9.1	Stoichiometry	226
9.2	Terminology for Applications of Stoichiometry	233
10	MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION	260
10.1	Species Material Balances	261
10.2	Element Material Balances	278
10.3	Material Balances Involving Combustion	283
11	MATERIAL BALANCE PROBLEMS INVOLVING MULTIPLE UNITS	305
12	RECYCLE, BYPASS, PURGE, AND THE INDUSTRIAL APPLICATION OF MATERIAL BALANCES	341
12.1	Introduction	342
12.2	Recycle without Chemical Reaction	347
12.3	Recycle with Chemical Reaction	355
12.4	Bypass and Purge	365
12.5	The Industrial Application of Material Balances	373
PART 3	<i>GASES, VAPORS, LIQUIDS, AND SOLIDS</i>	396
13	IDEAL GASES	401
13.1	The Ideal Gas Law	402
13.2	Ideal Gas Mixtures and Partial Pressure	412
13.3	Material Balances Involving Ideal Gases	416
14	REAL GASES: COMPRESSIBILITY	435
15	REAL GASES: EQUATIONS OF STATE	459
16	SINGLE COMPONENT TWO-PHASE SYSTEMS (VAPOR PRESSURE)	475
16.1	Phase Diagrams	476
16.2	Modeling and Predicting Vapor Pressure as a Function of Temperature	485

17	TWO-PHASE GAS-LIQUID SYSTEMS (SATURATION, CONDENSATION, AND VAPORIZATION)	509
17.1	Saturation	510
17.2	Condensation	514
17.3	Vaporization	525
18	TWO-PHASE GAS-LIQUID SYSTEMS (PARTIAL SATURATION AND HUMIDITY)	537
18.1	Terminology Involved for Partial Saturation	538
18.2	Material Balance Problems Involving Partial Saturation	544
19	THE PHASE RULE AND VAPOR-LIQUID EQUILIBRIA	560
19.1	The Gibbs Phase Rule	561
19.2	Vapor-Liquid Equilibria in Binary Systems	565
20	LIQUIDS AND GASES IN EQUILIBRIUM WITH SOLIDS	590
PART 4	ENERGY BALANCES	603
21	ENERGY: TERMINOLOGY, CONCEPTS, AND UNITS	607
21.1	The Terminology Associated with Energy Balances	608
21.2	Types of Energy	613
22	INTRODUCTION TO ENERGY BALANCES FOR PROCESSES WITHOUT REACTION	645
22.1	The Concept of the Conservation of Energy	646
22.2	Energy Balances for Closed, Unsteady-State Systems	648
22.3	Energy Balances for Closed, Steady-State Systems	655
22.4	Energy Balances for Open, Unsteady-State Systems	657
22.5	Energy Balances for Open, Steady-State Systems	666

23	CALCULATION OF ENTHALPY CHANGES	681
23.1	Phase Transitions	682
23.2	Heat Capacity Equations	690
23.3	Tables and Charts to Retrieve Enthalpy Values	699
23.4	Computer Databases	705
24	APPLICATION OF ENERGY BALANCES IN THE ABSENCE OF CHEMICAL REACTIONS	717
24.1	Simplifications of the General Energy Balance	718
24.2	The Strategy for Solving Energy Balance Problems	723
24.3	Application of the Energy Balance to Closed Systems	728
24.4	Application of the Energy Balance to Open Systems	735
25	ENERGY BALANCES: HOW TO ACCOUNT FOR CHEMICAL REACTION	763
25.1	The Standard Heat (Enthalpy) of Formation	764
25.2	The Heat (Enthalpy) of Reaction	769
25.3	Merging the Heat of Formation with the Sensible Heat of a Compound in Making an Energy Balance	780
25.4	The Heat of Combustion	785
26	ENERGY BALANCES THAT INCLUDE THE EFFECTS OF CHEMICAL REACTION	802
26.1	Analysis of the Degrees of Freedom to Include the Energy Balance with Reaction	803
26.2	Applications of Energy Balances in Processes that Include Reactions	806
27	IDEAL PROCESSES, EFFICIENCY, AND THE MECHANICAL ENERGY BALANCE	836
27.1	Ideal Reversible Processes	837
27.2	Efficiency	843
27.3	The Mechanical Energy Balance	848

28	HEATS OF SOLUTION AND MIXING	864
28.1	Heats of Solution, Dissolution, and Mixing	865
28.2	Introducing the Effects of Mixing into the Energy Balance	872
29	HUMIDITY (PSYCHROMETRIC) CHARTS AND THEIR USE	884
29.1	Terminology	885
29.2	The Humidity (Psychrometric) Chart	888
29.3	Applications of the Humidity Chart	897
 PART 5 SUPPLEMENTARY MATERIAL (ON THE ACCOMPANYING CD)		
30	ANALYSIS OF THE DEGREES OF FREEDOM IN A STEADY-STATE PROCESS	913
31	SOLVING MATERIAL AND ENERGY BALANCES USING PROCESS SIMULATORS (FLOWSHEETING CODES)	938
32	UNSTEADY-STATE MATERIAL AND ENERGY BALANCES	970
	APPENDICES	997
A	ANSWERS TO SELF-ASSESSMENT TESTS	007
B	ATOMIC WEIGHTS AND NUMBERS	1030
C	TABLE OF THE PITZER Z^0 AND Z^1 FACTORS	1031
D	PHYSICAL PROPERTIES OF VARIOUS ORGANIC AND INORGANIC SUBSTANCES	1036
E	HEAT CAPACITY EQUATIONS	1048
F	HEATS OF FORMATION AND COMBUSTION	1052
G	VAPOR PRESSURES	1057

Contents

xiii

H	HEATS OF SOLUTION AND DILUTION	1058
I	ENTHALPY-CONCENTRATION DATA	1059
J	THERMODYNAMIC CHARTS	1065
K	PHYSICAL PROPERTIES OF PETROLEUM FRACTIONS	1067
L	SOLUTION OF SETS OF EQUATIONS	1069
M	FITTING FUNCTIONS TO DATA	1085
N	ANSWERS TO SELECTED PROBLEMS	1089
	INDEX	1105



PREFACE

This book is intended to serve as an introduction to the principles and techniques used in the field of chemical, petroleum, and environmental engineering. Although the range of subjects deemed to be in the province of “chemical engineering” has broadened over the last decade, the basic principles involved in chemical engineering remain the same. This book lays a foundation of certain information and skills that can be repeatedly employed in subsequent courses as well as in professional life.

Our Motivation for Writing This Book

Far too many chemical engineering textbooks have become difficult, dry, and demoralizing for their readers. With this book, we have maintained a conversational style and detailed explanation of principles both in the text and examples to provide a readable yet comprehensive text. We have strived to maintain a suitable balance between understanding and developing skills. Our vision is to avoid comments (from a student about a different text) such as: “My text is useless, well not really, I use it to kill roaches in my room.”

Piaget has argued that human intelligence proceeds in stages from the concrete to the abstract and that one of the biggest problems in teaching is that the teachers are formal reasoners (using abstraction) while many students are still concrete thinkers or at best in transition to formal operational thinking. We believe that there is considerable truth in this viewpoint. Consequently, we initiate most topics with simple examples that illustrate the basic ideas. In this book the topics are presented

in order of assimilation. We start with easy material followed by more difficult material to give readers a “breather” before passing over each hump.

Assumed Prerequisites

The level of the book is directed to the first course in chemical engineering, which usually occurs in a student's sophomore year. We have assumed that you as a reader to have completed the second part of calculus and started organic chemistry. Familiarity with hand-held calculators is essential, but computer programming is not. Familiarity with PC software would be helpful, but is not critical.

Intended Audience

We believe that the main category of individuals who will use this book will be students of chemical engineering. However, the book is well designed for courses for nonchemical engineers as well as independent study, long-distance learning, and review for licensing examinations through its self-assessment features.

Our Objectives

This book is not an introduction to chemical engineering as a profession. We have focused instead on five general objectives in writing this book:

1. To introduce you to the principles and calculation techniques used in chemical engineering.
2. To acquaint you with what material and energy balances are, and how to formulate and solve them.
3. To assist you in learning efficient and consistent methods of problem solving so that you can effectively solve problems you will encounter after leaving school.
4. To offer practice in defining problems, collecting data, analyzing the data and breaking it down into basic patterns, and selecting pertinent information for application.
5. To review certain principles of applied physical chemistry.

In addition to focusing on the five above objectives, we expose you to background information on units and measurements of physical properties; basic laws about the behavior of gases, liquids, and solids; and some basic mathematical tools. Other ob-

jectives that an instructor may want to include in a course, such as programming and communication skills, information about professional activities, developing a professional attitude, establishing personal goals, developing social awareness, and so on, must be implemented from other sources. Economic feasibility, a major factor in engineering decision making, costing, and optimization, have been omitted because of lack of space.

We have not focused on using process simulation software to analyze and solve problems even though it is very good in exploring and handling “what if” questions as well as removing some of the drudgery in solving problems because

1. the pedagogy is too closely aligned to cookbook-style problem solving;
2. learning how to use the software with ease takes some time; and
3. development of a problem-solving strategy is taken out of the hands of the user by the software programmers. The software provides too much guidance for neophytes.

Organization and Scope of this Book

The major portion of the book comprises four parts:

Part 1. Background information (Chapters 1–5)

Part 2. Material balances (Chapters 6–12)

Part 3. Behavior of gases, liquids, and solids (Chapters 13–20)

Part 4. Energy balances (Chapters 21–29)

In addition, on the accompanying CD, Chapter 30 treats the degrees of freedom, Chapter 31 process simulators, and Chapter 32 unsteady state material and energy balances.

A series of appendices follow that include, in addition to tables and charts of physical properties, miscellaneous information you will find useful. Look at the Table of Contents for details.

In the CD that accompanies this book you will find several valuable tools:

1. Polymath: Software that solves equations, and can be used without reading any instructions.
2. Software to retrieve physical property data for over 740 compounds.
3. A Supplementary Problems Workbook containing 100 problems with complete detailed solutions, and another 100 problems with answers.
4. Descriptions of process equipment, and animations that illustrate the functions of the equipment.

5. Problem-solving suggestions including check lists to help you diagnose and overcome problem-solving difficulties you may experience.

To provide an appreciation of what processing equipment really looks like and how it works, in the files on the CD disk in the worked-out problems are numerous pictures of the equipment along with an explanation of their function and operation.

Problem Sets

We have included several categories of problems in the books to assist in self-study.

1. Self-assessment tests with answers (in Appendix A) follow each section.
2. Thought and discussion problems follow the self-assessment tests. Thought problems require reflection more than calculation. Discussion problems, which can be used as the basis of research, papers, and class discussions, pertain to broader issues and are more open ended.
3. Homework-type problems are listed at the end of each chapter, one-third of which have answers (in Appendix N). Each of the problems is rated 1 to 3 (using asterisks) to indicate the degree of difficulty, with 3 being the most difficult.
4. The CD contains more than 100 worked-out examples and another 100 problems with answers keyed to sections in the chapters in the text.

All of the examples and problems are designed to build your problem-solving skills.

Miscellaneous Useful Features in this Book

To make the book more usable and friendly, we have incorporated a number of beneficial features:

1. A list of contents at the beginning of each chapter.
2. A list of instructional objectives at the beginning of each chapter.
3. Important terms appear in **boldface** type.
4. A glossary has been placed at the end of each chapter.
5. Supplementary references that you can use to get additional information are listed at the end of each chapter.
6. Web sites containing information and links are listed at the end of each chapter.

7. The examples are simple and concrete so that the book is both teachable and useful for self instruction.
8. The chapter topics are independent but linked through a few principles.
9. The examples demonstrate a proven problem-solving strategy.

New Features in the Seventh Edition

The seventh edition is a completely rewritten and revised version of *Basic Principles and Calculations in Chemical Engineering*. Instead of five long chapters, the book is now comprised of 32 short chapters, each typically corresponding to one class session in a schedule of three meetings a week. New features include:

1. A consistent, sound strategy for solving material balance and energy balance problems, one can be used again and again as a framework for solving word problems, which is explained in Chapter 7. All of the examples in this book showing how to solve material and energy balances have been formulated according to this strategy.
2. The examples and problems in each chapter have been augmented to include expanded areas of importance to chemical engineers such as safety, semiconductor processing, and biotechnology.
3. The chapters on material balances have been revised to offer practice in finding out what the problem is, defining it, collecting data to be used in the problem, analyzing the information pertaining to the problem in order to relate it to what you know about similar problems, and, in effect, doing everything but testing the solution experimentally.
4. The extent of reaction has been added to the tools used to solve problems involving chemical reactions.
5. The degree of freedom analysis in solving problems has been emphasized and simplified.
6. A glossary has been added to each chapter.

On the CD that accompanies this book is

7. A new version of Polymath, a self-documented, widely used software package that runs on PCs and can solve linear, nonlinear, and differential equations as well as regression problems.
8. A new physical properties database that contains retrievable physical properties (such as vapor pressures and heat capacities and enthalpies for 740 compounds plus the steam tables).

ACKNOWLEDGMENTS

We are indebted to many former teachers, colleagues, and students who directly or indirectly helped in preparing this book, and in particular the present edition of it. Special thanks go to Chris Bailor for getting the manuscript to its final form, and to H. R. Heichelheim and Dale Slaback for their reviews of the manuscript. We also want to thank Professor C. L. Yaws for his kindness in making available the physical properties database that is the basis of the physical properties packages in the CD in the back of this book, and also thanks to Professors M. B. Cutlip and M. Shacham who graciously made the Polymath software available. Far too many instructors using the text have contributed their corrections and suggestions to list them by name. However, we do wish to express our appreciation for their kind assistance. Any further comments and suggestions for improvement of the book would be appreciated.

David M. Himmelblau
Austin, Texas

James B. Riggs
Lubbock, Texas

READ ME

Welcome to our book *Basic Principles and Calculations in Chemical Engineering*. Several tools exist in the book in addition to the basic text to aid you in learning its subject matter. **Don't neglect to use them.**

Learning Aids

1. Numerous examples worked out in detail to illustrate the basic principles.
2. A consistent strategy for problem solving that can be applied to any problem.
3. Figures, sketches, and diagrams to provide reinforcement of what you read.
4. A list of the specific objectives to be reached at the beginning of each chapter.
5. Self assessment tests at the end of each section, with answers so that you can evaluate your progress in learning.
6. A large number of problems at the end of each chapter with answers provided in Appendix N for about a third of them.
7. Thought and discussion problems that involve more reflection and consideration than the problem sets cited in #6 above.
8. An appendix containing data pertinent to the examples and problems.
9. Supplementary references for each chapter.
10. A glossary following each section.
11. A CD that includes some valuable accessories:

- a. Polymath—an equation-solving program that does not require any training to use.
 - b. Software that contains a physical properties database of over 700 compounds
 - c. A Supplementary Problems Workbook with over 100 completely solved problems and another 100 problems with answers.
 - d. The Workbook contains indexed descriptions of process equipment, and animations that illustrate the functions of the equipment. You can instantly access these pages if you want to look something up by clicking on the page number.
 - e. Problem-solving suggestions including check lists to diagnose and overcome problem-solving difficulties that you experience.
12. In the pocket in the back of the book is a set of steam tables (properties of water) both in SI and American Engineering units.

Scan through the book now to locate these features.

Good Learning Practices (Learning How to Learn)

You cannot put the same shoe on every foot.

Publilius Syrus

Those who study learning characteristics and educational psychologists say that people learn by practicing and reflecting, and not by watching and listening to someone else telling them what they are supposed to learn. “Lecturing is not teaching and listening is not learning.” You learn by doing.

Learning involves more than memorizing.

Do not equate memorizing with learning. Recording, copying, and outlining notes or the text to memorize problem solutions will be of little help in really understanding how to solve material and energy balance problems. Practice will help you to be able to apply your knowledge to problems that you have not seen before.

Adopt good learning practices.

You will find that skipping the text and jumping to equations or examples to solve problems may work sometimes, but in the long run will lead to frustration. Such a strategy is called “formula centered,” and is a very poor way to approach a problem-solving subject. By adopting it, you will not be able to generalize, each problem will be a new challenge, and the interconnections among essentially similar problems will be missed.

Various appropriate learning styles (information processing) do exist, hence you should reflect on what you do to learn, and adopt techniques best suited for you. Some students learn through thinking things out in solitary study. Others prefer to talk things through with peers or tutors. Some focus best on practical examples; others prefer abstract ideas. Sketches and graphs used in explanation usually appeal to most people. Do you get bored by going over the same ground? You might want to take a battery of tests to assess your learning style. Students often find such inventories interesting and helpful. Look in the CD that accompanies this book to read about learning styles.

Whatever your learning style, here are some suggestions to enhance learning that we feel are appropriate to pass on to you.

Suggestions to Enhance Learning

1. Each chapter in this book will require three or more hours to read, assimilate, and practice your skills in solving pertinent problems. Make allowance in your schedule so that you will have read the pertinent material **before** coming to class.
2. If you are enrolled in a class, work with one or more classmates, if permitted, to exchange ideas. But do not rely on someone to do your work for you.
3. Learn everyday. Keep up with the scheduled assignments—don't get behind because one topic builds on a previous one.
4. Seek answers to unanswered questions right away.
5. Employ active reading, that is, every 5 or 10 minutes stop for 1 or 2 minutes, and summarize what you have learned. Look for connecting ideas. Write a summary on paper if it helps.

Suggestions as to How to Use This Book Effectively

How can you make best use of this book? Read the objectives before and after studying each section. Read the text, and when you get to an example, first cover up the solution and try to solve the stated problem. Some people, those who learn by reading concrete examples, might look at the examples first and then read the text. After reading a section, solve the self-assessment problems at the end of the section. The answers are in Appendix A. After completing a chapter, solve a few of the problems listed at the end of the chapter. R. P. Feynman, the Nobel laureate in physics, made the point: "You do not know anything until you **have practiced**." Whether you solve the problems using hand calculators or computer **programs** is up to you, but use a systematic approach to formulating the **if**

proper solution. Use the supplement on the CD in the back of the book (print it out if you need to) as a source of examples of additional solved problems with which to practice solving problems.

This book functions as a savings account—what you put in you get out, with interest.



FREQUENTLY ASKED QUESTIONS

What Do Chemical Engineers Do?

Chemical engineering is an intriguing, challenging, and flexible profession. Chemical engineering graduates work in a wide variety of industries, as indicated in Table A.

TABLE A Initial Job Placement of Chemical Engineering Graduates in 2000–2001
in Percent (*Source: AIChE, NY, NY*).

Industry	BS	MS	PhD
Chemical	23.3	1.8	21.3
Fuels	15.7	7.6	10.6
Electronics	15.9	27.4	29.5
Food/Consumer Products	10.6	6.6	4.3
Materials	3.1	2.5	3.4
Biotechnology & Related Industries (Pharmaceuticals)	9.3	14.7	15.9
Pulp & Paper	2.1	1.5	1.5
Engineering Services			
Design & Construction	5.6	6.6	1.9
Research & Testing	1.8	4.1	3.4
Environmental Engineering	2.4	2.5	1.5
Business Services	5.8	2.0	2.9
Other Industries	3.9	2.5	3.9

In the industries listed in Table A, chemical engineers focus on design, operation, control, troubleshooting, research, management, and even politics, the latter because of environmental and economic concerns.

Some chemical engineers design processes and solve problems using their computing skills and specialist knowledge of reactions, separations, heat transfer, fluid flow, control, and economics. Others lead teams of experts from various disciplines in managing installations and directing plant operations. You will find chemical engineers use their expertise in management, marketing, information technology, business, and financial planning. If you want additional information, look at some of the web sites listed in Table B.

TABLE B Web Sites Providing Information on Chemical Engineering

<http://www.aiche.org>
<http://www.chemspy.com>
<http://www.j-edainc.com/Groups/ChemicalEngineering.htm>
<http://www.monstertrak.com>
<http://www.umin.che>

What Other Text Books Can I Read That Cover the Same Topics as This One?

Here are some of the more recent ones; many others were published in the period 1950–1980:

Felder, R.M., and R. W. Rousseau. *Elementary Principles of Chemical Processes*, 3rd ed., John Wiley, New York (2000).

Luyben, W.L., and L.A. Wenzen. *Chemical Process Analysis: Mass and Energy Balances*. Prentice-Hall, Englewood Cliffs, N.J. (1988).

Reklaitis, E. V., and D. R. Schneider. *Introduction to Material and Energy Balances*. John Wiley, New York (1983).

Shaheen, E. I. *Basic Practice of Chemical Engineering*. Houghton Mifflin, Palo Alto, CA (1975).

What Computer Codes Can Be Used to Solve the Equations Formulated in Homework Problems (and Examples)?

Software packages involving symbolic and numerical calculations along with graphics have over the last decade become essential tools for all engineering

great potential of computers is their capacity to do anything that can be described mathematically as a series of operations and logical decisions—theoretically. From a practical viewpoint, you should ask not merely whether it is feasible for a task to be performed on a computer, but whether it is sensible. Two questions should be asked in reaching a decision: (1) can the task be performed (or the problem solved) at all without the use of a computer; and (2) is it better or cheaper or faster to use a computer to solve a problem than a hand-held calculator (or no machine at all)?

Some commercial software that solves equations and provides graphics (and much more in many cases) in order of increasing difficulty in learning how to use is:

Polymath
TK solver
Mathcad
Excel
Matlab
Mathematica
Maple

You can find many of these codes installed on university computers, or purchase them at reasonable prices with an educational discount.

On the CD that accompanies this book you will find a software program called Polymath. This program solves linear equations, nonlinear equations, differential equations, and carries out linear and nonlinear regression (curve fitting). A significant advantage of Polymath is that you do not have to read an instruction manual to use it. You just look at the sample equations displayed on the screen and follow their format.

In addition, process simulators solve equations as part of their many other functions. Refer to Chapter 31 for examples of such codes. Most departments of chemical engineering have licenses for one or more of these process simulators, but they take some effort to learn how to use.

Where Can I Find More Examples of Problems and Their Solutions?

The CD that accompanies this book contains more than 100 additional examples of problems with their detailed solutions, and another 100 problems with answers. In addition, you can find numerous examples and problems with answers in the references cited above.

Where Can I Get Information and Data To Solve the Homework Problems if the Appropriate Data is Not in the Problem Statement, Appendix, or CD?

Accurate values of physical properties are needed in almost all phases of chemical engineering design and analysis. Various ways to obtain data for the physical properties of components besides the Internet are:

1. Employer's database
2. Design software (such as flowsheeting codes)
3. On-line databases
4. On-line bulletin boards/e-mail
5. Personal files and books
6. Departmental library
7. Employer's main library
8. Outside library
9. Technical magazines/newsletters
10. Professional society meetings
11. Trade association meetings
12. Continuing education courses
13. Other engineers in department
14. Outside consultants
15. Regulatory agencies
16. Raw material/equipment vendors
17. Clients/customers
18. Direct experimentation

Much of the data you want is available with little or no cost, particularly over the Internet. You will be interested in using physical property databases in one of three ways:

1. Retrieve an isolated value to be used in a calculation or in the calculation of other property values. Often a value is to be employed in hand calculations, or perhaps fed as input data to a computer program for further calculation.
2. Serve as a subroutine (such as a physical properties library) to another computer program to provide physical property data for process calculations.
3. Provide interactive capabilities for the rapid rendering of physical properties of substances of interest for parametric studies of process units, that is, "ask what if."

Many of the materials we talk about and use every day are not pure compounds, but nevertheless you can obtain information about the properties of such materials. Data on materials such as coal, coke, petroleum products, and natural gas—which are the main sources of energy in this country—are available in reference books and handbooks. Examine Tables C, D, and E.

TABLE C Sources of Physical Property Data

-
- American Chemical Society, TAPD, 17,000 compounds, on disk, ACS, Washington, D.C. (1994).
- American Chemical Society, *Chemical Abstracts Service*, ACS, Washington, D.C. (Continuing printed, microform, and on-line electronic information service with over 20 million abstracts.)
- American Gas Association, *Fuel Flue Gases*, AGA, New York (1941).
- American Petroleum Institute, *Technical Data Book—Petroleum Refining*, New York (1970).
- Beilstein On-line; properties of 3.5 million chemical compounds. Also CD-Disk, ongoing.
- Dechema, *Chemistry Data Series*, Deutsche Gesellschaft für Chemisches Apparatuswesen e.v., Berlin, Germany. (Continuing series on physical and thermodynamic properties.) 10,000 compounds.
- DeLevie, R. *How to Use Excel in Analytical Chemistry and General Scientific Data Analysis*, Cambridge Univ. Press, New York (2001).
- Design Institute for Physical Property Data, DIPPR, gives properties and prediction equations for over 1,400 compounds; available as printed book, tape, on-line; Amer. Inst. Chemical Engineers, New York, on-going.
- Engineering Sciences Data Unit Ltd., *International Data Series*, London. (Continuing series of data and equations.)
- Environmental Chemicals Data Information Network, Ecdin, data on 25,000 substances, registration of 103,000. Distributed by Technical Database Services (TDS).
- Handbook of Physics and Chemistry*, CRC Press, Boca Raton, FL., annual editions. Also on the Web.
- Lange's Handbook of Chemistry and Physics*, McGraw-Hill, New York; issued periodically. Also on the Web.
- Lin, C.T., et al., "Data Bank for Synthetic Fuels"; *Hydrocarbon Process*, p. 229 (May 1980).
- National Engineering Laboratories, PPDS2, 1,600 compounds; Glasgow, UK, ongoing.
- Natural Gas Processors Suppliers Association, *Engineering Data Book*, Tulsa, Okla. (Continuing editions.)
- Perry, R. H., D. W. Green, and J. O. Maloney. *Perry's Chemical Engineer's Handbook*, 7th ed., McGraw-Hill, New York (2000). Also on the Web.
- Poling, B. D., J. M. Prausnitz, and J. O'Connell. *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, New York (2002).
- PTB Laboratory, *Chemsafe*, 1,600 gases, liquids, and dusts that can explode; distributed on disk, tape, on-line; Braunschweig, Germany (1995).
- STN International, *STN Express*, provides access to many databases on-line. Chemical Abstracts Service, Columbus, Ohio, continuing.
- Thermodynamic Research Center, Texas A&M University, *TRC Vapor Pressure Data Profile for 5,500 chemicals*; on disk (1994).
- Yaws, C. L. *Chemical Properties Handbook*, McGraw-Hill, New York (1999).
-

TABLE D Professional Journals

Archival journals (in English)

AIChE Journal
Canadian Journal of Chemical Engineering
Chemical Engineering Communications
Chemical Engineering Journal (Lausanne)
Chemical Engineering Science
Computers and Chemical Engineering
Industrial & Engineering Chemistry Research
Journal of Chemical and Engineering Data
Journal of Chemical Engineering of Japan
Journal of Chemical Technology and Biotechnology

Other journals and magazines

Chemical Engineer (London)
Chemical Engineering
Chemical Engineering Progress
Chemical Processing
Chemical Technology
Chemistry and Industry (London)

Table E lists some valuable web sites that have links to hundreds of other sites.

TABLE E Data Source on the Web

<http://www.chemicalonline.com>
<http://www.chempute.com/main.htm>
<http://www.cheresources.com>
<http://www.che.ufl.edu/www-che>
http://www.deb.uminho.pt/fontes/chem_eng/education/chee_links.htm
<http://www.knovel.com>
<http://www.mwsoftware.com/dragon/desc.html>
<http://myplant.com>
<http://www.retallick.com/resources/netresrc.html>
<http://www.shef.ac.uk/uni/academic/A-C/cpe/mpitt/chemengs.html>

PART 1

INTRODUCTION

CHAPTER	PAGE
1 Dimensions, Units, and Their Conversion	5
2 Moles, Density, and Concentration	42
3 Choosing a Basis	78
4 Temperature	89
5 Pressure	99

Part 1 begins your introduction to chemical engineering calculations by reviewing certain topics underlying the main principles to be discussed. You have already encountered most of these concepts in your basic chemistry and physics courses. Why, then, the need for a review? First, from experience we have found it necessary to restate these familiar basic concepts in a somewhat more precise and clearer fashion; second, you will need practice to develop your ability to analyze and work engineering problems. If you encounter new material as you go through these chapters, or if you flounder over little gaps in your skills or knowledge of old material, you should devote extra attention to the chapters by solving extra problems in the set that you will find at the end of each chapter. To read and understand the principles discussed in these chapters is relatively easy; to apply them to different unfamiliar situations is not. An engineer becomes competent in his or her profession by mastering the techniques developed by one's predecessors—thereafter comes the time to pioneer new ones.

*What I hear, I forget;
What I see, I remember;
What I do, I understand.*

Confucius

Part 1 begins with a discussion of units, dimensions, and conversion factors, and then goes on to review some terms you should already be acquainted with, including:

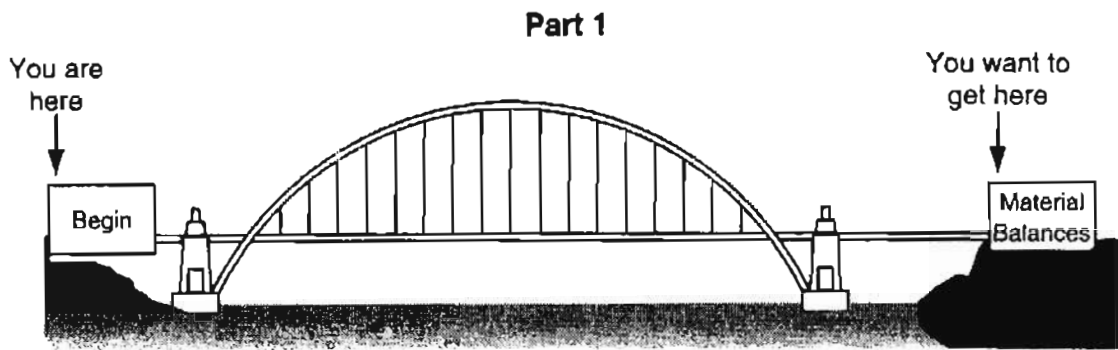


Figure Part 1.1 The bridge to success.

- a. Mole and mole fraction
- b. Density and specific gravity
- c. Measures of concentration
- d. Temperature
- e. Pressure

A firm grasp of this information as presented in the next five chapters will help guarantee “plug-and-play” acquisition of the information in the remaining chapters. You will find that adding new ideas and techniques will be as easy as copying and pasting images in a computer. Consider the following story.

One night a group of nomads were preparing to retire for the evening when suddenly they were surrounded by a great light. They knew they were in the presence of a celestial being. With great anticipation, they awaited a heavenly message of great importance that they knew must be especially for them.

Finally, the voice spoke.

“Gather as many pebbles as you can. Put them in your saddle bags. Travel a day’s journey and tomorrow night will find you glad and it will find you sad.”

After the light departed, the nomads shared their disappointment and anger with each other. They had expected the revelation of a great universal truth that would enable them to create wealth, health, and purpose for the world. But instead they were given a menial task that made no sense to them at all. However, the memory of the brilliance of their visitor caused each one to pick up a few pebbles and deposit them in their saddle bags while voicing their displeasure.

They traveled a day’s journey and that night while making camp, they reached into their saddle bags and discovered every pebble they had gathered had become a diamond. They were glad they had diamonds. They were sad they had not gathered more pebbles.*

*Schlatter, J. W., quoted in *A Second Helping of Chicken Soup for the Soul*, J. Canfield and M. Hansen (eds.), Health Communications, Deerfield Beach, FL (1995).

SUPPLEMENTARY REFERENCES

- Felder, R. M., and R. W. Rousseau. *Elementary Principles of Chemical Processes*, 3rd ed., John Wiley, N.Y. (2000).
- Luyben, W. L., and L. A. Wenzen. *Chemical Process Analysis: Mass and Energy Balances*. Prentice-Hall, Eaglewood Cliffs, N.J. (1988).
- Reklaitis, E. V., and D. R. Schneider. *Introduction to Material and Energy Balances*. John Wiley, N.Y. (1983).
- Shaheen, E. I. *Basic Practice of Chemical Engineering*. Houghton Mifflin, Palo Alto, CA (1975).

CHAPTER 1

DIMENSIONS, UNITS, AND THEIR CONVERSION

1.1 Units and Dimensions	6
1.2 Operations with Units	11
1.3 Conversion of Units and Conversion Factors	14
1.4 Dimensional Consistency (Homogeneity)	21
1.5 Significant Figures	24
1.6 Validation of Problem Solutions	30

Your objectives in studying this chapter are to be able to:

1. Understand and explain the difference between dimensions and units.
2. Add, subtract, multiply, and divide units associated with numbers.
3. Specify the basic and derived units in the SI and American Engineering (AE) systems for mass, length, volume, density, and time, and their equivalents.
4. Convert one set of units in a function or equation into another equivalent set for mass, length, area, volume, time, and force.
5. Explain the difference between weight and mass.
6. Define and know when to use the gravitational conversion factor g_c .
7. Apply the concepts of dimensional consistency to determine the validity of an equation or function.
8. Employ an appropriate number of significant figures in your calculations.

"Take care of your units and they will take care of you."

Anonymous

At some time in every engineer's life comes the exasperating sensation of frustration in problem solving. Somehow, the answers or the calculations do not come out as expected. Often this outcome arises because of errors in the handling of units.

The use of units along with the numbers in your calculations requires more attention than you probably have been giving to your computations in the past. In addition, you will discover that checking the consistency of units in your equations will prove to be a valuable tool that will reduce the number of errors you commit when performing engineering calculations.

Looking Ahead

In this chapter we review the SI and American Engineering systems of units, show how conversions between units can be accomplished efficiently, and discuss the concept of dimensional homogeneity (consistency). We also provide some comments with respect to the number of significant figures to use in your calculations.

1.1 Units and Dimensions

Engineers and scientists have to be able to communicate not only with words but also by carefully defined numerical descriptions. Read the following news report that appeared in the *Wall Street Journal*, June 6, 2001, on page A22:

SEOUL, South Korea—A mix up in the cockpit over whether altitude guidance was measured in feet or meters led to the crash of a Korean Air Lines McDonnell Douglas MD-11 freighter soon after takeoff in Shanghai in April 1999, investigators said.

The crash killed all three crew-members. Five people on the ground were killed and 40 more were injured when the plane went down in light rain onto a construction site near Shanghai's Hongqiao Airport.

According to a summary of the crash report released by South Korean authorities, a Chinese air-traffic controller directed the pilots to an altitude of 1,500 meters (4,950 feet). The plane was climbing rapidly to that level when the co-pilot told the pilot he thought the instructed height was 1,500 feet, equivalent to 455 meters. The international aviation industry commonly measures altitude in feet, and the confusion led the pilot to conclude the jet was almost 1,000 meters too high, so he quickly moved the controls to lower the plane. As the plane descended, the pilot realized the error but couldn't correct the mistake in time.

South Korea's Ministry of Construction and Transportation said Korean Air Lines would lose the right to serve the Seoul-Shanghai cargo route for at least two years because of errors by the pilots. Korean Air Lines said it would appeal the decision . . .

Now you can understand the point of defining your quantities carefully so that your communications are understood.

1.1-1 What Are Units and Dimensions and How Do They Differ?

Dimensions are our basic concepts of measurement such as *length, time, mass, temperature*, and so on; **units** are the means of expressing the dimensions, such as *feet* or *centimeters* for length, and *hours* or *seconds* for time. By attaching units to all numbers that are not fundamentally dimensionless, you get the following very practical benefits:

- a. diminished possibility of errors in your calculations,
- b. reduced intermediate calculations and time in problem solving,
- c. a logical approach to the problem rather than remembering a formula and substituting numbers into the formula,
- d. easy interpretation of the physical meaning of the numbers you use.

In this book you will use the two most commonly used systems of units:

1. **SI**, formally called *Le Systeme Internationale d'Unites*, and informally called **SI** or more often (redundantly) the **SI** system of units.
2. **AE**, or *American Engineering* system of units, not to be confused with what is called the *U.S. Conventional System (USCS)* nor the *English* system of units.

The **SI** system has certain advantages over the **AE** system in that fewer names are associated with the dimensions, and conversion of one set of units to another is easier, but in the United States the **AE** system has deep roots. Most modern computer programs (e.g., process simulators) allow the use of either or mixed sets of units.

Dimensions and their respective units are classified as fundamental or derived:

- **Fundamental** (or basic) dimensions/units are those that can be measured independently and are sufficient to describe essential physical quantities.
- **Derived** dimensions/units are those that can be developed in terms of the fundamental dimensions/units.

Tables 1.1 and 1.2 list both basic, derived, and alternative units in the **SI** and **AE** systems. Figure 1.1 illustrates the relation between the basic dimensions and some of the derived dimensions. For example, squaring length results in area, cubing length results in volume, and dividing volume by time gives the volumetric flow rate. What are the dimensions of the mass flux (mass flow rate per unit area)? Can you add the appropriate lines in Figure 1.1?

The distinction between uppercase and lowercase letters should be followed even if the symbol appears in applications where the other lettering is in uppercase style. Unit abbreviations have the same form for both the singular and plural, and they are not followed by a period (except in the case of inches). One of the best fea-

TABLE 1.1 SI Units Encountered in This Book

Physical Quantity	Name of Unit	Symbol for Unit*	Definition of Unit
<i>Basic SI Units</i>			
Length	metre, meter	m	
Mass	kilogramme, kilogram	kg	
Time	second	s	
Temperature	kelvin	K	
Molar amount	mole	mol	
<i>Derived SI Units</i>			
Energy	joule	J	$\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \rightarrow \text{Pa} \cdot \text{m}^3$
Force	newton	N	$\text{kg} \cdot \text{m} \cdot \text{s}^{-2} \rightarrow \text{J} \cdot \text{m}^{-1}$
Power	watt	W	$\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-3} \rightarrow \text{J} \cdot \text{s}^{-1}$
Density	kilogram per cubic meter		$\text{kg} \cdot \text{m}^{-3}$
Velocity	meter per second		$\text{m} \cdot \text{s}^{-1}$
Acceleration	meter per second squared		$\text{m} \cdot \text{s}^{-2}$
Pressure	newton per square meter, pascal		$\text{N} \cdot \text{m}^{-2}$, Pa
Heat capacity	joule per (kilogram · kelvin)		$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
<i>Alternative Units</i>			
Time	minute, hour, day, year	min, h, d, y	
Temperature	degree Celsius	°C	
Volume	litre, liter (dm^3)	L	
Mass	tonne, ton (Mg), gram	t, g	

* Symbols for units do not take a plural form, but plural forms are used for the unabbreviated names. Non-SI units such as day (d), liter or litre (L), and ton or tonne (t) are legally recognized for use with SI.

tures of the SI system is that (except for time) units and their multiples and submultiples are related by standard factors designated by the prefix indicated in Table 1.3.

When a compound unit is formed by multiplication of two or more other units, its symbol consists of the symbols for the separate units joined by a centered dot (e.g., N · m for newton meter). The dot may be omitted in the case of familiar units such as watt-hour (symbol Wh) if no confusion will result, or if the symbols are separated by exponents, as in $\text{N} \cdot \text{m}^2 \text{kg}^{-2}$. Hyphens should not be used in symbols for compound units. Positive and negative exponents may be used with the symbols for the separate units either separated by a solidus or multiplied by using negative powers (e.g., m/s or $\text{m} \cdot \text{s}^{-1}$ for meters per second). **However, we do not use the center dot for multiplication in this text.** A dot can easily get confused with a period or

TABLE 1.2 American Engineering (AE) System Units Encountered in This Book

Physical Quantity	Name of Unit	Symbol
<i>Some Basic Units</i>		
Length	foot	ft
Mass	pound (mass)	lb _m
Time	second, minute, hour, day	s, min, h (hr), day
Temperature	degree Rankine or degree Fahrenheit	°R or °F
Molar amount	pound mole	lb mol
<i>Derived Units</i>		
Force	pound (force)	lb _f
Energy	British thermal unit, foot pound (force)	Btu, (ft)(lb _f)
Power	horsepower	hp
Density	pound (mass) per cubic foot	lb _m /ft ³
Velocity	feet per second	ft/s
Acceleration	feet per second squared	ft/s ²
Pressure	pound (force) per square inch	lb _f /in. ² , psi
Heat capacity	Btu per pound (mass) per degree F	Btu/(lb _m)(°F)

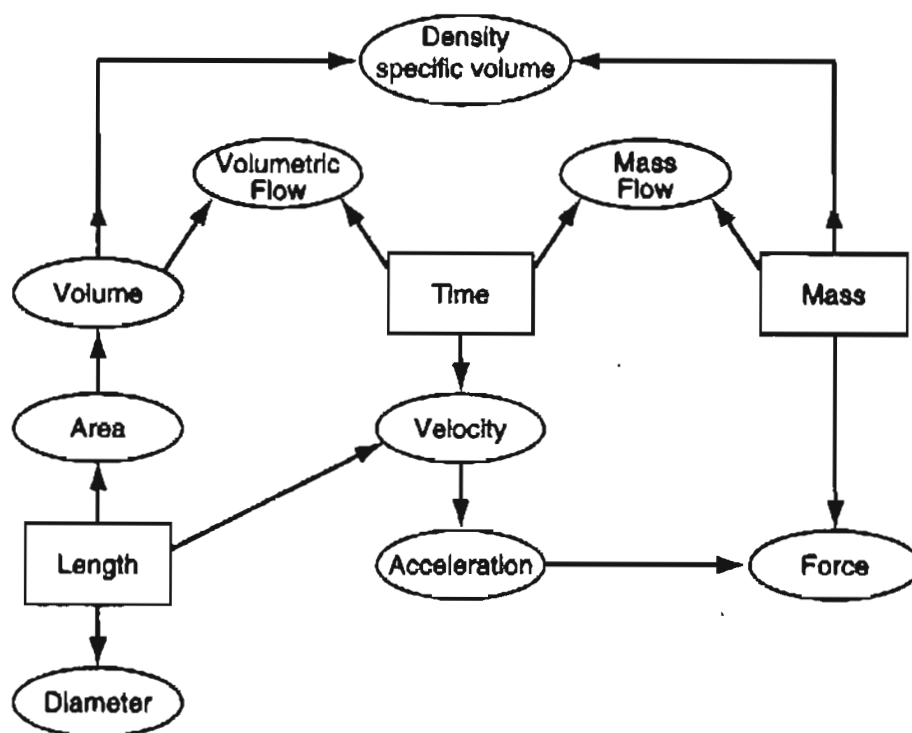
**Figure 1.1** Relation between the basic dimensions (in boxes) and various derived dimensions (in ellipses).

TABLE 1.3 SI Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^9	<i>giga</i>	G	10^{-1}	<i>deci</i>	d
10^6	<i>mega</i>	M	10^{-2}	<i>centi</i>	c
10^3	<i>kilo</i>	k	10^{-3}	<i>milli</i>	m
10^2	<i>hecto</i>	h	10^{-6}	<i>micro</i>	μ
10^1	<i>deka</i>	da	10^{-9}	<i>nano</i>	n

missed entirely in handwritten calculations. Instead, we will use parentheses or vertical rules, whichever is more convenient, for multiplication and division. Also, the SI convention of leaving a space between groups of numbers such as 12 650 instead of inserting a comma, as in 12,650, will be ignored to avoid confusion in handwritten numbers.

Frequently Asked Questions

1. Is the SI system of units the same as the metric system? The answer is no. SI differs from versions of the metric system (such as CGS) in the number of basic units and in the way the basic units are defined.
2. What is the major difference between the AE and USCS systems? In the USCS system the pound force is a basic unit and the pound mass a derived unit.
3. What does ms mean: millisecond or meter seconds? Mind your use of meters! The letters ms mean millisecond; the combination (m) (s) or $m \cdot s$ would mean meter seconds. Similarly, 1 Mm is not 1 mm! Notation such as cm^2 , meaning square centimeters, frequently has to be written as $(\text{cm})^2$ to avoid confusion.

SELF-ASSESSMENT TEST

(Answers to the self-assessment tests are listed in Appendix A.)

Questions

1. Which of the following best represents the force needed to lift a heavy suitcase:
 - a. 25 N
 - b. 25 kN
 - c. 250 N
 - d. 250 kN?
2. Pick the correct answer(s); a watt is
 - a. one joule per second
 - b. equal to $1 (\text{kg})(\text{m}^2)/\text{s}^2$

- c. the unit for all types of power
 - d. all of the above
 - e. none of the above
3. Is kg/s a basic or derived unit in SI?
 4. In the *IEEE Spectrum* (Jan. 2001, pp. 14–16) an article on building out the wireless Internet proposed a cell for each 0.05 km^2 . Does this seem reasonable?

Problems

1. Prepare a table in which the rows are: length, volume, mass, and time. Make two columns, one for the SI and the other for the AE system of units. Fill in each row with the respective name of the unit, and in a third column show the numerical equivalency (i.e., $1 \text{ ft} = 0.3048 \text{ m}$).
2. Classify the following units as correct or incorrect units in the SI system:
 - a. nm
 - b. °K
 - c. sec
 - d. N/mm
 - e. $\text{kJ}/(\text{s})(\text{m}^3)$

Thought Problem

1. What volume of material will a barrel hold?

Discussion Problem

1. In a letter to the editor, the letter writer says:

I believe SI notation might be improved so as to make it mathematically more useful by setting SI-sanctioned prefixes in **boldface** type. Then one would write, $1 \text{ c} = 10 \text{ m}$ without any ambiguity [$\text{c} = 10^{-2}$, $\text{m} = 10^{-3}$] and the meaning of “mm” would be at once clear to any mathematically literate, if scientifically illiterate, citizen, namely either 10^{-3} m [mm], 10^{-6} [mm], or (after Gauss and early algebraists) m^2 [mm].

With respect to the “mm” problem and remarks regarding the difference between “one square millimeter” [$(\text{mm})^2$] and “one mili squaremeter” [$\text{m}(\text{m}^2)$], these difficulties are analogous to the confusion between a “camel’s-hair brush” and a camel’s hair-brush.”

What do you think of the author’s proposal?

1.2 Operations with Units

Answers to a question such as: how much is $2 + 2$ can sometimes be debatable. You might state 4. A bad calculator might show 3.99999. What about $9 + 5$? Can the answer for $9 + 5 = 2$ possibly be correct? Hint: Look at a wall clock.

Every freshman knows that what you get from adding apples to oranges is fruit salad! The rules for handling units are essentially quite simple:

1.2-1 Addition, Subtraction, Equality

You can add, subtract, or equate numerical quantities only if the associated units of the quantities are the same. Thus, the operation

$$5 \text{ kilograms} + 3 \text{ joules}$$

cannot be carried out because the units as well as the dimensions of the two terms are different. The numerical operation

$$10 \text{ pounds} + 5 \text{ grams}$$

can be performed (because the dimensions are the same, mass) *only* after the units are transformed to be the same, either pounds, grams, or ounces, or some other mass unit.

1.2-2 Multiplication and Division

You can multiply or divide unlike units at will such as

$$50(\text{kg})(\text{m})/(\text{s})$$

but you cannot cancel or merge units unless they are identical. Thus, $3 \text{ m}^2/60 \text{ cm}$ can be converted to $3 \text{ m}^2/0.6 \text{ m}$, and then to 5 m , but in m/s^2 , the units cannot be cancelled or combined. In summary, units contain a significant amount of information that cannot be ignored. They also serve as guides in efficient problem solving, as you will see shortly.

Frequently Asked Question

How should you handle mathematical operations or units such as sine, log, or exponential? To be specific, if you take the log of 16 m^2 and treat the number and units as a product, then you would have

$$\log(16\text{m}^2) = \log(16) + 2 \log(\text{m})$$

Various awkward ways and tricks of handling quantities such as $2 \log(\text{m})$ have been proposed (see, e.g., M. Karr and D. B. Loveman, "Incorporation of Units into Programming Languages," *Comm. ACM*, **21**, 385–391 [1978]). We prefer for simplicity to require that a variable be transformed or scaled to be dimensionless before you apply nonlinear operations such as log. For example, for a pipe of radius R with

units of m , we would develop a dimensionless variable r^* , a fraction, for a distance r from the axis also in m , to operate on

$$r^* = \frac{rm}{Rm}$$

so that

$$\log r^* = \log r + \log m - \log R - \log m = \log r - \log R = \log \frac{r}{R}$$

Can you suggest what the scaling could be for a square duct? What if the units of r are not in meters?

EXAMPLE 1.1 Dimensions and Units

Add the following:

- (a) 1 foot + 3 seconds
- (b) 1 horsepower + 300 watts

Solution

The operation indicated by

$$1 \text{ ft} + 3 \text{ s}$$

has no meaning since the dimensions of the two terms are not the same. One foot has the dimensions of length, whereas 3 seconds has the dimensions of time. In the case of

$$1 \text{ hp} + 300 \text{ watts}$$

the dimensions are the same (energy per unit time), but the units are different. You must transform the two quantities into like units, such as horsepower or watts, before the addition can be carried out. Since $1 \text{ hp} = 746 \text{ watts}$,

$$746 \text{ watts} + 300 \text{ watts} = 1046 \text{ watts}$$

SELF-ASSESSMENT TEST

Questions

1. Answer the following questions yes or no. Can you
 - a. divide ft by s?
 - b. divide m by cm?
 - c. multiply ft by s?

- d. divide ft by cm?
 - e. divide m by (deg) K?
 - f. add ft and s?
 - g. subtract m and (deg) K
 - h. add cm and ft?
 - i. add cm and m^2 ?
 - j. add 1 and 2 cm?
2. Why is it not possible to add 1 ft and 1 ft^2 ?
 3. Explain how to accommodate operations such as exp and ln on a number accompanied by units.

Problems

1. Add 1 cm and 1 m.
2. Subtract 3 ft from 4 yards.
3. Divide $3 m^{1.5}$ by $2 m^{0.5}$.
4. Multiply 2 ft by 4 lb.

Discussion Problem

1. There seems to be two schools of thought concerning how to take the logarithm of a number that has associated dimensions. The proponents of the first school hold that taking the logarithm of a dimensioned variable is a perfectly acceptable procedure, one that leads to a dimensionless result regardless of the dimensions of the original variable. The opposing school is that taking the logarithm of a dimensioned variable is improper, and even meaningless, and the variable should be in dimensionless form before the logarithm is taken. What side do you believe is correct? Explain the reasons for your choice.

1.3 Conversion of Units and Conversion Factors

Mistakes are the usual bridge between inexperience and wisdom.

Phyllis Theroux, *Night Lights*

Columbus had many of the qualities that would appeal to today's venture capitalists. He was an experienced seafarer, prepared detailed written proposals for his ventures, and was dedicated and sincere. King John of Portugal, who rejected his first proposal in 1484, regarded him as boastful, fanciful, and overimaginative. His Portuguese experts believed that the distance to the Indies was 10,000 (U.S.) miles, four times Columbus's estimate of 2,500 (U.S.) miles. Both the experts and Columbus knew he had to travel about 68° of longitude, but Columbus apparently interpreted the Arabic literature in which the measure for 1° was $56 \frac{2}{3}$ miles (U.S.) as

ancient Italian miles, which are equal to modern 37 U.S. miles. Consequently, he thought that 68° was about 2,500 U.S. miles, whereas the correct distance was about 3900 U.S. miles.

As another example of a serious conversion error, in 1999 the Mars Climate Orbiter was lost because engineers failed to make a simple conversion from English units to SI, an embarrassing lapse that sent the \$125 million craft fatally close to the Martian surface.

As a prospective engineer you must be careful of handling all sorts of units, and be able to convert a given set of units to another set with ease.

As you probably already know, the procedure for converting one set of units to another is simply to multiply any number and its associated units by ratios termed *conversion factors* to arrive at the desired answer and its associated units. Conversion factors are statements of equivalent values of different units in the same system or between systems of units used in the form of ratios. You can view a pair of (correct) conversion factors as quantities that form a ratio so that multiplying a term by the ratio is essentially the same as multiplying the term by 1.

On the inside of the front cover of this book you will find tables of commonly used conversion factors. You can locate many others in handbooks and on the Internet. Some of the references to consult can be found at the end of the chapter. Memorize a few of the common ones to save time looking them up. It will take you less time to use conversion factors you know than to look up better ones. Some web sites do the conversions for you! In the physical property software on the CD in the back of this book you can insert almost any units you want in order to retrieve property values. Nevertheless, being able to make conversions by yourself is important.

In this book, to help you follow the calculations and emphasize the use of units, we frequently make use of a special format in the calculations, as shown below. Consider the following problem:

If a plane travels at twice the speed of sound (assume that the speed of sound is 1100 ft/s), how fast is it going in miles per hour?

We formulate the conversion as follows

$$\begin{array}{c}
 2 \times \frac{1100 \text{ ft}}{\text{s}} \left| \frac{1 \text{ mi}}{5280 \text{ ft}} \right| \frac{60 \text{ s}}{1 \text{ min}} \left| \frac{60 \text{ min}}{1 \text{ hr}} \right. \\
 \frac{\text{ft}}{\text{s}} \quad \quad \frac{\text{mi}}{\text{s}} \quad \quad \frac{\text{mi}}{\text{min}}
 \end{array}$$

Note the format of the calculations. We have set up the calculations with vertical lines separating each ratio. These lines retain the same meaning as a \cdot , or parenthesis, or a multiplication sign (\times) placed between each ratio. We will use this formulation frequently in this text to enable you to keep clearly in mind the significance of units in problem solving. We recommend that you always write down the units next to the as-

sociated numerical value (unless the calculation is very simple) until you become quite familiar with the use of units and can carry them in your head.

Another convenient way you can keep track of the net units in an equation is to strike through the units that can be cancelled as you proceed with the calculations. For example:

$$\frac{2(1100)\cancel{\text{ft}}}{\cancel{\text{s}}} \left| \frac{1 \text{ mile}}{5280 \cancel{\text{ft}}} \right| \frac{60 \cancel{\text{s}}}{1 \cancel{\text{min}}} \left| \frac{60 \cancel{\text{min}}}{1 \text{ hr}} \right|$$

At any stage in the conversion you can determine the consolidated net units and see what conversions are still required. If you want, you can do this formally, as shown above, by drawing slanted lines below the dimensional equation and writing the consolidated units on these lines; or you can do it by eye, mentally canceling and accumulating the units; or you can strike out pairs of identical units as you proceed. Consistent use of units along with numbers throughout your professional career will assist you in avoiding silly mistakes such as converting 10 centimeters to inches by multiplying by 2.54:

$$\frac{10 \text{ cm}}{1 \text{ in.}} \left| \frac{2.54 \text{ cm}}{1 \text{ in.}} \right| \neq 25.4 \text{ in.}, \text{ instead of } \frac{10 \text{ cm}}{2.54 \text{ cm}} \left| \frac{1 \text{ in.}}{2.54 \text{ cm}} \right| = 3.94 \text{ in.}$$

By three methods we may learn wisdom: First, by reflection, which is noblest; second, by imitation, which is easiest; and third by experience, which is the bitterest.

Confucius

Now let's look at an example.

EXAMPLE 1.2 Conversion of Units

- (a) Convert 2 km to miles.
- (b) Convert 400 in.³/day to cm³/min.

Solution

- (a) One way to carry out the conversion is to look up a direct conversion factor, namely 1.61 km = 1 mile:

$$\frac{2 \text{ km}}{1.61 \text{ km}} \left| \frac{1 \text{ mile}}{1.61 \text{ km}} \right| = 1.24 \text{ mile}$$

Another way is to use conversion factors you know

$$\frac{2 \text{ km}}{1 \text{ km}} \left| \frac{10^5 \text{ cm}}{1 \text{ km}} \right| \left| \frac{1 \text{ in.}}{2.54 \text{ cm}} \right| \left| \frac{1 \text{ ft}}{12 \text{ in.}} \right| \left| \frac{1 \text{ mile}}{5280 \text{ ft}} \right| = 1.24 \text{ mile}$$

$$(b) \frac{400 \text{ in.}^3}{\text{day}} \left| \frac{2.54 \text{ cm}}{1 \text{ in.}} \right|^3 \left| \frac{1 \text{ day}}{24 \text{ hr}} \right| \left| \frac{1 \text{ hr}}{60 \text{ min}} \right| = 4.55 \frac{\text{cm}^3}{\text{min}}$$

In part (b) note that not only are the numbers in the conversion of inches to centimeters raised to a power, but the units also are raised to the same power.

EXAMPLE 1.3 Nanotechnology

Nanosized materials have become the subject of intensive investigation in the last decade because of their potential use in semiconductors, drugs, protein detectors, and electron transport. Nanotechnology is the generic term that refers to the synthesis and application of such small particles. An example of a semiconductor is ZnS with a particle diameter of 1.8 nanometers. Convert this value to (a) dm (decimeters) and (b) inches.

Solution

$$(a) \frac{1.8 \text{ nm}}{1} \left| \frac{10^{-9} \text{ m}}{1 \text{ nm}} \right| \left| \frac{10 \text{ dm}}{1 \text{ m}} \right| = 1.8 \times 10^{-8} \text{ dm}$$

$$(b) \frac{1.8 \text{ nm}}{1} \left| \frac{10^{-9} \text{ m}}{1 \text{ nm}} \right| \left| \frac{39.37 \text{ in.}}{1 \text{ m}} \right| = 7.09 \times 10^{-8} \text{ in.}$$

In the AE system the conversion of terms involving pound **mass** and pound **force** deserve special attention. Let us start the discussion with Newton's Law:

$$F = Cma \quad (1.1)$$

where F = force

C = a constant whose numerical value and units depend on those selected for F , m , and a

m = mass

a = acceleration

In the SI system in which the unit of force is defined to be the Newton (N) when 1 kg is accelerated at 1 m/s², a conversion factor $C = 1 \text{ N}/(\text{Kg})(\text{m})/\text{s}^2$ must be introduced to have the force be 1 N:

$$F = \frac{1 \text{ N}}{\frac{(\text{kg})(\text{m})}{\text{s}^2}} \left| \frac{1 \text{ kg}}{\tilde{m}} \right| \left| \frac{1 \text{ m}}{\tilde{a} \text{ s}^2} \right| = 1 \text{ N} \quad (1.1)$$

Because the numerical value associated with the conversion factor is 1, the conversion factor seems simple, even nonexistent, and the units are ordinarily ignored.

In the AE system an analogous conversion factor is required. However, to make the numerical value of the force and the mass be essentially the same at the earth's surface, if a mass of 1 lb_m is hypothetically accelerated at g ft/s², where g is the acceleration that would be caused by gravity (about 32.2 ft/s² depending on the location of the mass), we can make the force be 1 lb_f by choosing the proper numerical value and units for the conversion factor C :

$$F = \left(\frac{1(\text{lb}_f)(s^2)}{32.174(\text{lb}_m)(\text{ft})} \right) \left(\frac{1 \text{ lb}_m}{\tilde{m}} \left| \frac{g \text{ ft}}{\tilde{g} s^2} \right. \right) = 1 \text{ lb}_f \quad (1.2)$$

A numerical value of 1/32.174 has been chosen for the numerical value in the conversion factor because 32.174 is the numerical value of the average acceleration of gravity (g) (9.80665 m/s²) at sea level at 45° latitude when g is expressed in ft/s². The acceleration caused by gravity, you may recall, varies by a few tenths of 1% from place to place on the surface of the earth but is quite different on the surface of the moon.

The inverse of the conversion factor with the numerical value 32.174 included is given the *special symbol* g_c

$$g_c = 32.174 \frac{(\text{ft})(\text{lb}_m)}{(s^2)(\text{lb}_f)}$$

that you will see included in equations in some texts to remind you that the numerical value of the conversion factor is not a unity. To avoid confusion, we will not place g_c in the equations in this book because we will be using both SI and AE units. You will discover that the use of g_c is essential in the AE system when you need a conversion factor to adjust units when both lb_m and lb_f are involved in a calculation, or when lb_f has to be transformed to lb_m in a unit such as psia (lb_f/in.²).

In summary, you can see that the AE system has the convenience that the numerical value of a pound mass is also that of a pound force if the numerical value of the ratio g/g_c is equal to 1, as it is approximately in most cases. No one gets confused by the fact that a person who is 6 feet tall has only two feet. **In this book, we will not subscript the symbol lb with m (for mass) or f (for force) unless it becomes essential to do so to avoid confusion. We will always mean by the unit lb without a subscript the quantity pound mass. But never forget that the pound (mass) and pound (force) are not the same units in the AE system even though we speak of pounds to express force, weight, or mass.**

What is the difference between mass and weight? When someone says they weigh 100 kg, or 200 pounds, how can that statement be correct when you know that **weight** is a force, not a mass, equal to the opposite of the force required to support a

mass (consult some of the references at the end of this chapter for a more precise definition of weight)? To avoid confusion, just interpret the statement as follows: a person or object weighs as much as a mass of 100 kg, or 200 pounds, would weigh, if measured by a force scale.

Some Useful Trivia Concerning Conversion

A U.S. frequent-flier mile is not the same as a U.S. mile—the former is a nautical mile (1.85 km), whereas the latter is 1.61 km. In the AE system $1 \text{ m} = 39.37 \text{ in.}$, whereas for U.S. land survey applications it is $2 \times 10^{-6} \text{ in.}$ shorter.

EXAMPLE 1.4 A Conversion Involving Both lb_m and lb_f

What is the potential energy in $(\text{ft})(\text{lb}_f)$ of a 100 lb drum hanging 10 ft above the surface of the earth with reference to the surface of the earth?

Solution

The first thing to do is read the problem carefully. What are the unknown quantities? The potential energy (PE) is unknown. What are the known quantities? The mass and the height of the drum are known. How are they related? You have to look up the relation unless you recall it from physics:

$$\text{Potential energy} = P = mgh$$

Assume that the 100 lb means 100 lb mass; g = acceleration of gravity = 32.2 ft/s^2 . Figure E1.4 is a sketch of the system.

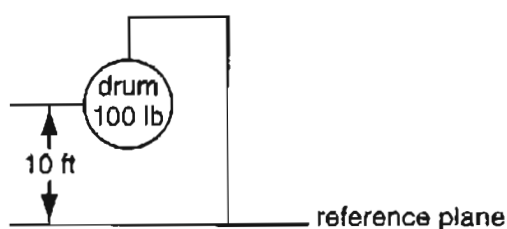


Figure E1.4

Now substitute the numerical values of the variables into the equation and perform the necessary unit conversions.

$$P = \frac{100 \text{ lb}_m}{1} \left| \frac{32.2 \text{ ft}}{\text{s}^2} \right| \left| \frac{10 \text{ ft}}{1} \right| \frac{(\text{s}^2)(\text{lb}_f)}{32.174(\text{ft})(\text{lb}_m)} = 1000 (\text{ft})(\text{lb}_f)$$

Notice that in the ratio of 32.2 ft/s^2 divided by $32.174[(\text{ft})(\text{lb}_m)]/[(\text{s}^2)(\text{lb}_f)]$, the numerical values are almost equal. Many engineers would solve the problem by saying that $100 \text{ lb} \times 10 \text{ ft} = 1000 (\text{ft})(\text{lb})$ without realizing that, in effect, they are canceling out the numbers in the g/g_c ratio, and that the lb in the solution means lb_f .

EXAMPLE 1.5 Conversion of Units Associated with Biological Materials

In biological systems, enzymes are used to accelerate the rates of certain biological reactions. Glucoamylase is an enzyme that aids in the conversion of starch to glucose (a sugar that cells use for energy). Experiments show that $1 \mu\text{g mol}$ of glucoamylase in a 4% starch solution results in a production rate of glucose of $0.6 \mu\text{g mol}/(\text{mL})(\text{min})$. Determine the production rate of glucose for this system in the units of $\text{lb mol}/(\text{ft}^3)(\text{day})$.

Solution

Basis: 1 min

$$\begin{aligned} & \frac{0.6 \mu\text{g mol}}{(\text{mL})(\text{min})} \left| \frac{1 \text{ g mol}}{10^6 \mu\text{g mol}} \right| \left| \frac{1 \text{ lb mol}}{454 \text{ g mol}} \right| \left| \frac{1000 \text{ mL}}{1 \text{ L}} \right| \left| \frac{1 \text{ L}}{3.531 \times 10^{-2} \text{ ft}^3} \right| \left| \frac{60 \text{ min}}{\text{hr}} \right| \left| \frac{24 \text{ hr}}{\text{day}} \right| \\ &= 0.0539 \frac{\text{lb mol}}{(\text{ft}^3)(\text{day})} \end{aligned}$$

SELF-ASSESSMENT TEST

Questions

1. What is g_c ?
2. Is the ratio of the numerator and denominator in a conversion factor equal to unity?
3. What is the difference, if any, between pound force and pound mass in the AE system?
4. Could a unit of force in the SI system be kilogram force?
5. Contrast the procedure for converting units within the SI system with that for the AE system.
6. What is the weight of a one pound mass at sea level? Would the mass be the same at the center of Earth? Would the weight be the same at the center of Earth?
7. What is the mass of an object that weighs 9.80 kN at sea level?

Problems

1. What are the value and units of g_c in the SI system?
2. Electronic communication via radio travels at approximately the speed of light (186,000 miles/second). The edge of the solar system is roughly at Pluto, which is 3.6×10^9 miles from Earth at its closest approach. How many hours does it take for a radio signal from Earth to reach Pluto?

3. Determine the kinetic energy of one pound of fluid moving in a pipe at the speed of 3 feet per second.
4. Convert the following from AE to SI units:
 - a. $4 \text{ lb}_m/\text{ft}$ to kg/m
 - b. $1.00 \text{ lb}_m/(\text{ft}^3)(\text{s})$ to $\text{kg}/(\text{m}^3)(\text{s})$
5. Convert the following

$$1.57 \times 10^{-2} \text{ g}/(\text{cm})(\text{s}) \text{ to } \text{lb}_m/(\text{ft})(\text{s})$$

6. Convert 1.1 gal to ft^3 .
7. Convert 1.1 gal to m^3 .

Thought Problems

1. Comment as to what is wrong with the following statements from a textbook:
 - a. Weight is the product of mass times the force of gravity.
 - b. A 67-kg person on earth will weigh only 11 kg on the moon.
 - c. If you have 1 g of water at 4°C that has a volume of 1.00 mL, you can use the ratio $1.00 \text{ g water}/4^\circ\text{C}$ as a conversion factor.
2. In the conversion tables in *Perry's Handbook* (5th ed.) is a row showing that the factor 0.10197 converts newtons to kilograms. Can this be correct?

Discussion Problem

1. In spite of the official adoption of the SI system of units in most countries, people still buy 10 kg of potatoes and inflate automobile tires to a value in kg (or kg/cm^2). Why does this usage occur?

1.4 Dimensional Consistency (Homogeneity)

Now that we have reviewed some background material concerning units and dimensions, we can immediately make use of this information in a very practical and important application. **A basic principle states that equations must be dimensionally consistent.** What the principle means is that each term in an equation must have the same net dimensions and units as every other term to which it is added, subtracted, or equated. Consequently, dimensional considerations can be used to help identify the dimensions and units of terms or quantities in an equation.

The concept of dimensional consistency can be illustrated by an equation that represents the pressure/volume/temperature behavior of a gas, and is known as van der Waals's equation, an equation that is discussed in more detail in Chapter 15:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

Inspection of the equation shows that the constant a must have the units of [(pressure)(volume)²] for the expression in the first set of parentheses to be consistent throughout. If the units of pressure are atm and those of volume are cm³, a will have the units of [(atm)(cm)⁶]. Similarly, b must have the same units as V , or in this particular case the units of cm³. If T is in K , what must be the units of R ? Check your answer by looking up R inside the front cover of the book. All equations must exhibit dimensional consistency.

EXAMPLE 1.6 Dimensional Consistency

Your handbook shows that microchip etching roughly follows the relation

$$d = 16.2 - 16.2e^{-0.021t} \quad t < 200$$

where d is the depth of the etch in microns (micrometers, μm) and t is the time of the etch in seconds. What are the units associated with the numbers 16.2 and 0.021? Convert the relation so that d becomes expressed in inches and t can be used in minutes.

Solution

After you inspect the equation that relates d as a function of t , you should be able to reach a decision about the units associated with each term on the righthand side of the equation. Both values of 16.2 must have the associated units of microns (μm). The exponential must be dimensionless so that 0.021 must have the associated units of s^{-1} . To carry out the conversion, look up suitable conversion factors inside the front cover of this book and multiply so that the units are converted from 16.2 μm to inches, and 0.021 t / s to t / min .

$$\begin{aligned} d_{\text{in}} &= \frac{16.2 \mu\text{m}}{10^6 \mu\text{m}} \left| \frac{1 \text{ m}}{39.37 \text{ in.}} \right| \left[1 - \exp \left(\frac{-0.021}{\text{s}} \left| \frac{60 \text{ s}}{1 \text{ min}} \right| t_{\text{min}} \right) \right] \\ &= 6.38 \times 10^{-4} (1 - e^{-1.26 t_{\text{min}}}) \text{ inches} \end{aligned}$$

As you proceed with the study of chemical engineering, you will find that groups of symbols may be put together, either by theory or based on experiment, that have no net units. Such collections of variables or parameters are called **dimensionless** or **nondimensional groups**. One example is the Reynolds number (group) arising in fluid mechanics.

$$\text{Reynolds number} = \frac{D\nu\rho}{\mu} = N_{RE}$$

where D is the pipe diameter, say in cm; ν is the fluid velocity, say in cm/s; ρ is the fluid density, say in g/cm³; and μ is the viscosity, say in centipoise, units that can be converted to g/(cm)(s). Introducing the consistent set of units for D , ν , ρ , and μ into $D\nu\rho / \mu$, you will find that all the units cancel out so that the numerical value of 1 is the result of the cancellation of the units.

$$\frac{\text{cm}}{\text{s}} \left| \frac{\text{cm}}{\text{s}} \right| \frac{\text{g}}{\text{cm}^3} \left| \frac{(\text{cm})(\text{s})}{\text{g}} \right|$$

EXAMPLE 1.7 Interesting Example of Dimensional Consistency

Explain without differentiating why the following differentiation cannot be correct:

$$\frac{d}{dx} \sqrt{1 + (x^2/a^2)} = \frac{2ax}{\sqrt{1 + (x^2/a^2)}}$$

where x is length and a is a constant.

Solution

Observe that x and a must have the same units because the ratio $\frac{x^2}{a^2}$ must be dimensionless (because 1 is dimensionless).

Thus, the lefthand side of the equation has units of $\frac{1}{x}$ (from d/dx). However, the righthand side of the equation has units of x^2 (the product of ax).

Consequently, something is wrong as the equation is not dimensionally consistent.

SELF-ASSESSMENT TEST

Questions

1. Explain what dimensional consistency means in an equation.
2. Explain why the so-called dimensionless group has no net dimensions.
3. If you divide all of a series of terms in an equation by one of the terms, will the resulting series of terms be dimensionless?
4. How might you make the following variables dimensionless:
 - a. Length (of a pipe).
 - b. Time (to empty a tank full of water).

Problems

1. An orifice meter is used to measure the rate of flow of a fluid in pipes. The flow rate is related to the pressure drop by the following equation

$$u = c \sqrt{\frac{\Delta P}{\rho}}$$

where u = fluid velocity

Δp = pressure drop (force per unit area)

ρ = density of the flowing fluid

c = constant

What are the units of c in the SI system of units?

2. The thermal conductivity k of a liquid metal is predicted via the empirical equation

$$k = A \exp(B/T)$$

where k is in $J/(s)(m)(K)$ and A and B are constants. What are the units of A and B ?

Thought Problems

1. Can you prove the accuracy of an equation by checking it for dimensional consistency?
2. Suppose that some short time after the "Big Bang" the laws of nature turned out to be different than the laws currently used. In particular, instead of $pV = nRT$, a different gas law arose, namely $pVT = nR$. What comments do you have about such an equation?

Discussion Problem

1. In a letter criticizing an author's equation, the writer said:
The equation for kinetic energy of the fluid
is not dimensionally consistent. I suggest the modification

$$KE = mv^2 / 2g_c$$

in which g_c is introduced. Then the units in the equation will not be $(ft/s)^2$, which are the wrong units for energy.

What do you think of the comment in the letter?

1.5 Significant Figures

Decimals have a point.

Unknown

You have probably heard the story about the Egyptian tour guide who told the visitors that the pyramid they beheld in awe was 5013 years old. "Five thousand and

thirteen said a visitor!" "How do you know?" "Well, said the guide, when I first began working here 13 years ago, I was told the pyramid was 5000 years old."

What do you believe about the accuracy of a statement in a travel brochure in which you read that a mountain on a trip is 8000 m (26,246 ft high)?

Responsible physical scientists and engineers agree that a measurement should include three pieces of information:

- a. the magnitude of the variable being measured
- b. its units
- c. an estimate of its uncertainty

The last is likely to be either disassociated from the first two or ignored completely. If you have no idea of the accuracy of a measurement or a number, a conservative approach is to imply that the last digit is known within upper and lower bounds. For example, 1.43 indicates a value of 1.43 ± 0.005 , meaning that the value can be deemed to be between 1.425 and 1.435. Another interpretation of 1.43 is that it means 1.43 ± 0.01 .

What should you do when you add, subtract, multiply, and divide numbers that have associated uncertainty?

The accuracy you need for the results of a calculation depends on the proposed application of the results. The question is: How close is close enough? For example, in income tax forms you do not need to include cents, whereas in a bank statement cents (two decimals) are included. In engineering calculations, if the cost of inaccuracy is great (failure, fire, downtime, etc.), knowledge of the uncertainty in the calculated variables is vital. On the other hand, in determining how much fertilizer to put on your lawn in the summer, being off by 10 to 20 pounds out of 100 lb is not important.

Several options (besides common sense) exist in establishing the degree of certainty in a number. Three common decision criteria are: (1) absolute error, (2) relative error, and (3) statistical analysis.

1. First, consider the **absolute error** in a number. You have to consider two cases:

- a. numbers with a decimal point, and
- b. numbers without a decimal point.

For case (a), suppose we assume that the last significant figure in a number represents the associated uncertainty. Thus, the number 100.3 carries along the implication of 100.3 ± 0.05 , meaning 100.3 lies in the interval between 100.25 to 100.35. Thus, 100.3 would have what is termed four significant figures. For case (a), if the number is 100.300, we will presume that additional significant figures of accuracy exist so that 100.300 will have six significant figures. (Be aware that some textbooks and authors do not attribute significance to the trailing zeros on the righthand

side of a decimal point.) The rationale behind attributing additional significant figures to the trailing zeros is that they would not be added to 100.3 unless there was a reason for displaying additional accuracy. As an example, rounding the number 100.2997 to retain only six significant figures would give 100.300.

For case (b), if a number is stated without a decimal point, such as 201,300, we will assume that the trailing zeros (after the 3) do not imply any additional accuracy beyond four significant figures.

When you multiply or divide numbers, generally you should retain in your final answer the lowest number of significant figures that occur among all of the numbers involved in the calculations even though you carry along 10 or 20 digits during the calculations themselves. For example, we will treat the product $(1.47)(3.0926) = 4.54612$ as having only three significant figures because 1.47 has only three significant figures. The answer should be truncated to 4.55 to avoid suggesting any greater precision in the result of the multiplication.

When you add or subtract numbers, generally you should retain in your final answer the number of significant digits as determined by the error interval of the largest of the numbers. For example, in the addition

$$\begin{array}{r} 110.3 \\ + 0.038 \\ \hline 110.338 \end{array}$$

common sense would say to state the answer as 110.3. You should not have more than four significant figures in the sum. This decision reflects what is revealed by a more detailed examination of the error bounds imputed to the two numbers:

Upper Bound	Lower Bound
$110.3 + 0.05 = 110.35$	$110.3 - 0.05 = 110.25$
$0.038 + 0.0005 = \underline{0.0385}$	$0.038 - 0.005 = \underline{0.0375}$
110.3885	110.2875

The midpoint of these two numbers is 110.338.

Absolute errors are easy to track and compute, but they can lead to gross distortions in the specified uncertainty of a number. For example, let's divide 98 by 93.01. You can get

$$\begin{aligned} \frac{98}{93.01} &= 1.1 \\ &= 1.05 \\ &= 1.054 \\ &= 1.0537 \end{aligned}$$

What do you think about applying the rule that states that the number of significant digits in the least precise number (two significant digits here because 98 has two significant figures) should be the number of significant digits retained in the answer? If you apply this rule, the calculated answer is 1.1, clearly a distortion of the true error in the numbers because 98 ± 1 has an error of only about 1%, whereas the result, 1.1 ± 0.1 , has an error of about 10%! Certainly 1.0537 indicates too great a precision so that the choice should either be 1.05 or 1.054. Which do you think is better?

2. Perhaps the use of **relative error** can often be a better way to decide how many significant figures to retain in your answers. Suppose you divide one number by another number close to it such as $1.01/1.09 = 0.9266$, and select 0.927 as the answer. The uncertainty in the answer based on the absolute error analysis is $0.001/0.927$, or about 0.1%, whereas $(0.01/1.09)100$, or about a 1% uncertainty, existed in the original numbers. Should the relative uncertainty of the answer be fixed at about 1%, that is, truncate the answer to 0.93 rather than 0.927? Such would be the case if you applied the concept of relative error. The decision is up to you. In any case, avoid increasing the precision of your answer very much over the precision in your measurements or data when presenting results of calculations. You do have to use some common sense in applying the concept of relative error to scales that use both relative and absolute units. For example, suppose the measured error in a temperature of 25°C is 1°C , or 4%. Can you reduce the error by changing the temperature to kelvin, so that the error becomes $(1/298)100 = 0.33\%$? Of course not.

3. A more rigorous and more complicated third way to treat uncertainty in numbers is to apply statistics in the calculations. What is involved is the concept of confidence limits for the starting numbers in a calculation, and the propagation of errors step by step through each stage of the calculations to the final result. But even a statistical analysis is not exact because we deal with nonlinear ratios of numbers. Refer to a book on statistics for further information about this approach.

In this book we base most answers on absolute error because such a choice is convenient, but will often show one or two extra figures in intermediate calculations as you should. (The numbers in your calculator are not a Holy Writ!). Keep in mind that some numbers are exact, such as the $\frac{1}{2}$ in $\text{KE} = \frac{1}{2}mv^2$ and the 2 in the superscript for the operation of square. You will also encounter integers such as 1, 2, 3, and so on, which in some cases are exact (2 reactors, 3 input streams) but in other cases are shortcut substitutes for presumed very accurate measurements in problem solving (3 moles, 10 kg).

Given a mass such as 10 kg, in which the number does not have a decimal point, despite our remarks above about trailing zeros, you can infer that quite a few significant figures apply to the mass, particularly in relation to the other values of

the parameters stated in an example or problem, because you can easily measure a mass to a level of mg. You will also occasionally encounter fractions such as $2/3$, which can be treated as 0.6667 in relation to the accuracy of other values in a problem. In this text for convenience we will use 273 K for the temperature equivalent to 0°C instead of 273.15 K, thus introducing an absolute error of 0.15 degrees. This is such a small error relative to the other known or presumed errors in your calculations that it can be neglected in almost all instances. Keep in mind, however, that in addition, subtraction, multiplication, and division, all of the errors that you introduce propagate into the final answer.

Feel free to round off parameters such as $\pi = 3.1416$, $\sqrt{2} = 1.414$, or Avogadro's number $N = 6.02 \times 10^{23}$. In summary, be sure to round off your answers to problems to a reasonable number of significant figures even though numbers are carried out to 10 or more digits in your computer or calculator in the intermediate calculations.

EXAMPLE 1.8 Retention of Significant Figures

If 20,100 kg is subtracted from 22,400 kg, is the answer of 2,300 kg good to four significant figures?

Solution

If you note that 22,400, 20,100, and 2,300 have no decimal points after the righthand zero, how many significant figures can you attribute input to 22,400 and 20,100? By applying the absolute error concept you can conclude that the number of significant figures is three. Scientific notation makes this decision clearer

$$\begin{array}{r} 2.24 \times 10^4 \text{ kg} \\ -2.01 \times 10^4 \text{ kg} \\ \hline 0.23 \times 10^4 \text{ kg} \end{array}$$

and the result retains two significant figures.

On the other hand if a decimal point were placed in each number thus, 22,400. and 20,100., indicating that the last zero was significant, then the answer of 2,300. would be valid to four significant figures.

From the viewpoint of relative error, 22,400 has an error of about $1/2\%$ ($1/224$) as does 20,100 ($1/201$), whereas 2,300 has an error of about 5% ($1/23$). Should relative error have been used to establish the number of significant figures to be retained? Can you add a 0 to the right of 0.23 to give a relative error of ($1/230$) or about $1/2\%$? No. But what about giving the answer as $230. \times 10^3$?

EXAMPLE 1.9 Micro-dissection of DNA

A stretch-and-positioning technique on a carrier layer can be used for dissection and acquisition of an electrostatically positioned DNA strand. A device to do the micro-dissection consists of a glass substrate on which a sacrificial layer, a DNA carrier layer, and a pair of electrodes are deposited. The DNA is electrostatically stretched and immobilized onto the carrier layer with one of its molecular ends aligned on the electrode edge. A cut is made through the two layers with a stylus as a knife at an aimed portion of the DNA. By dissolving the sacrificial layer, the DNA fragment on the piece of carrier can be recovered on a membrane filter. The carrier piece can then be melted to obtain the DNA fragment in solution.

If the DNA is stretched out to a length of 48kb, and a cut made with a width of 3 μm , how many base pairs (bp) should be reported in the fragment? Note: 1 kb is 1000 base pairs (bp), and 3 kb = 1 μm .

Solution

Superficially the conversion is

$$\frac{3 \mu\text{m}}{1 \mu\text{m}} \left| \frac{3 \text{ kb}}{1 \mu\text{m}} \right| \frac{1000 \text{ bp}}{1 \text{ kb}} = 9000 \text{ bp}$$

However, because the measurement of the number of molecules in a DNA fragment can be determined to 3 or 4 significant figures in a thousand, and the 3 μm reported for the cut may well have more than 1 associated significant figure, the precision in the 9000 value may actually be better if the cut were determined to have a value of 3.0 or 3.00 μm .

SELF-ASSESSMENT TEST**Questions**

1. Why can the use of absolute error in determining the number of significant digits be misleading?
2. How can you avoid a significant loss of precision in carrying out calculations involving many repetitive operations (such as addition, multiplication, and so on)?
3. Will adding a decimal point to a reported number that does not have a decimal point, such as replacing 12,600 with 12,600., improve the precision of the number?

Problems

1. Identify the number of significant figures for each of the following numbers:

3.0

23

0.353

1,000

1,000.

1,000.0

2. What is the correct sum and the number of significant digits when you add (a) 5750 and 10.3? (b) 2.000 and 0.22?
3. Convert the water flow rate of 87.0 kg of water having a density of 1000 kg/m³ per minute to the units of gal/hr, giving the answer in the proper number of significant figures.
4. A computer chip made in Japan presumably costs \$78. The calculation to convert from yen to dollars was made as follows:

$$\left(\frac{10,000 \text{ yen}}{1 \text{ computer chip}} \right) \left(\frac{\$ 1.00}{128 \text{ yen}} \right) = \$ 78/\text{computer chip}$$

Is the number of significant digits shown in the answer correct?

5. What is the answer to: 78.3 – 3.14 – 0.388?

Thought Problems

1. Is 6 5/8 inches equivalent to (a) 5 1/8? (b) 6.375 inches?
2. When you want to calculate the weight of 6 silicon chips each weighing 2.35 g, is the answer good only to one significant figure, i.e., that of 6?
3. A textbook mentions the quantity of reactant as being 100 mL. How would you decide on the number of significant figures to associate with the quantity of reactant?

Discussion Problem

1. In a report of the crew laying fiber optics cable, the results for the month were listed as follows:

3000 ft
4120 ft
1300 ft
<u>2100 ft</u>
10,520 ft

How many significant figures would you attribute to the sum?

1.6 Validation of Problem Solutions

If a mistake is not a steppingstone, it is a mistake.

Eli Siegel

Validation (sometimes referred to as verification) means checking that your problem solution is satisfactory, and possibly assessing to some extent your problem-solving procedures. By satisfactory we mean correct or close enough. Since presumably you do not know the solution before you solve the problem, trying to

check your result with the unknown makes severe demands on your problem-solving skills. Unless you can compare your answer with a known one, such as the answers given in the Appendix to this and other books, what can you do? Here is a list of suggestions. (We will not consider statistical analysis.) The extent to which you can pursue a validation depends on the time you have available and the cost.

1. Repeat the calculations, possibly in a different order.
2. Start with the answer and perform the calculations in reverse order.
3. Review your assumptions and procedures. Make sure two errors do not cancel each other.
4. Compare numerical values with experimental data or data in a database (handbooks, the Internet, textbooks).
5. Examine the behavior of the calculation procedure. For example, use another starting value and check that the result changed appropriately.
6. Assess whether the answer is reasonable given what you know about the problem and its background.

The moment you have worked out an answer, start checking it—it probably isn't right.

Right Answers, *Computers and Automation*, p. 20 (September 1969)

SELF-ASSESSMENT TEST

Questions

1. Will using a calculator or computer help reduce numerical errors in your calculations?
2. What other ways of validating your answers to a problem can you suggest in addition to the one cited in Section 1.6?
3. Suppose you convert the amount of solid CaCl_2 in a 100 mL beaker with a net weight measured in grams to pounds, and get 2.41 lb. How would you go about checking the validity of this result?

Problems

1. Check the answer in the following calculation by starting with the answer to get the value for the original starting quantity. B is the molar density in cm^3 per gram mole of a compound, MW is the molecular weight of the compound, and ρ is the mass density of the compound in grams per cm^3 .

$$\frac{B}{\text{cm}^3} \left| \frac{\rho \text{ g mol}}{\text{cm}^3} \right| \left| \frac{1 \text{ ft}^3}{\rho \text{ lb}_m} \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 \left(\frac{1 \text{ m}}{35.31 \text{ ft}} \right)^3 \right| \left| \frac{1 \text{ lb}_m}{454 \text{ g}} \right| \frac{\text{MW g}}{1 \text{ g mol}} = (62.38)(\text{MW})B$$

B is the value of the variable and has the units of cm^3 . Do you get B?

Looking Back

In this chapter we have reviewed the essential background you need to become skilled in converting units, applying the concept of dimensional consistency in your work, and reporting numerical values with an appropriate number of significant digits.

GLOSSARY OF NEW WORDS

Absolute error Error in a number that is a fixed value.

AE American Engineering system of units.

Conversion of units Change of units from one set to another.

Derived units Units developed in terms of the fundamental units.

Dimensional consistency Each term in an equation must have the same set of net dimensions.

Dimensionless group A collection of variables or parameters that has no net dimensions (units).

Dimensions The basic concepts of measurement such as length or time.

Force A derived unit for the product of the mass and the acceleration.

Fundamental units Units that can be measured independently.

Mass A basic dimension for the amount of material.

Nondimensional group See Dimensionless group.

Pound force The unit of force in the AE system.

Pound mass The unit of mass in the AE system.

Relative error Fraction or percent error for a number.

SI *Le Systeme Internationale d'Unites* (SI system of units).

Units Method of expressing a dimension such as ft or hour.

Validation Determination that the solution to a problem is correct.

Weight A force opposite to the force required to support a mass (usually in a gravitational field).

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the FAQ in the front material, the following are pertinent:

1. Bhatt, B. I., and S. M. Vora. *Stoichiometry (SI Units)*, Tata McGraw-Hill, New Delhi (1998).

2. Horvath, A. L. *Conversion Tables in Science and Engineering*, Elsevier, New York (1986).
3. Luyben, W. L., and L. A. Wentzel. *Chemical Process Analysis: Mass and Energy Balances*, Prentice-Hall, Englewood Cliffs, N. J. (1988).
4. National Institute of Standards. *The International System of Units (SI)*, NIST Special Publ. No. 330, U.S. Department of Commerce, Gaithersburg, MD 20899 (1991).
5. Reilly, P. M. "A Statistical Look at Significant Figures," *Chem. Eng. Educ.* 152–155 (Summer 1992).
6. Vatavuk, W. M. "How Significant Are Your Figures," *Chem. Eng.* 97 (August 18, 1986).

Web Sites

<http://chemengineer.about.com>

<http://www.chemistrycoach.com/tutorials-2.html>

<http://www.ex.ac.uk/cimt/dictunit/dictunit.htm>

<http://mcgraw-hill.knovel.com/perrys>

<http://www.retallick.com/resources/netresrc.html>

<http://www.shef.ac.uk/uni/academic/A-C/cpe/mpitt/chemengs.html>

PROBLEMS

(The asterisks denote the degree of difficulty, *** being the most difficult.)

- *1.1 Carry out the following conversions:
 - (a) How many m^3 are there in $1.00(\text{mile})^3$?
 - (b) How many gal/min correspond to $1.00 \text{ ft}^3/\text{s}$?
- *1.2 Convert
 - (a) $0.04 \text{ g}/(\text{min})(\text{m}^3)$ to $\text{lb}_\text{m}/(\text{hr})(\text{ft}^3)$.
 - (b) $2 \text{ L}/\text{s}$ to ft^3/day .
 - (c) $\frac{6(\text{in})(\text{cm}^2)}{(\text{yr})(\text{s})(\text{lb}_\text{m})(\text{ft}^2)}$ to all SI units.
- *1.3 In a article describing an oil-shale retorting process, the authors say the retort: "could be operated at a solids mass flux well over $1,000 \text{ lb}/(\text{h})(\text{ft}^2)$ ($48\text{k Pa}/\text{h}$) . . ." In several places they speak of the grade of their shale in the mixed units " 34 gal (129 L)/ton." Does their report make sense?
- *1.4 Convert the following:
 - (a) $60.0 \text{ mi}/\text{hr}$ to ft/sec .
 - (b) $50.0 \text{ lb}/\text{in}^2$ to kg/m^2 .
 - (c) $6.20 \text{ cm}/\text{hr}^2$ to nm/sec^2 .

***1.5** The following test will measure your SIQ. List the correct answer.

- (a) Which is the correct symbol?
 (1) nm (2) °K
 (3) sec (4) N/mm
- (b) Which is the wrong symbol?
 (1) MN/m² (2) GHz/s
 (3) kJ/(s)(m³) (4) °C/M/s
- (c) Atmospheric pressure is about:
 (1) 100 Pa (2) 100 kPa
 (3) 10 MPa (4) 1 GPa
- (d) The temperature 0°C is defined as:
 (1) 273.15°K (2) Absolute zero
 (3) 273.15 K (4) The freezing point of water
- (e) Which height and mass are those of a petite woman?
 (1) 1.50 m, 45 kg (2) 2.00 m, 95 kg
 (3) 1.50 m, 75 kg (4) 1.80 m, 60 kg
- (f) Which is a recommended room temperature in winter?
 (1) 15°C (2) 20°C
 (3) 28°C (4) 45°C
- (g) The watt is:
 (1) One joule per second (2) Equal to 1 kg · m²/s³
 (3) The unit for all types of power (4) All of the above
- (h) What force may be needed to lift a heavy suitcase?
 (1) 24 N (2) 250 N
 (3) 25 kN (4) 250 kN

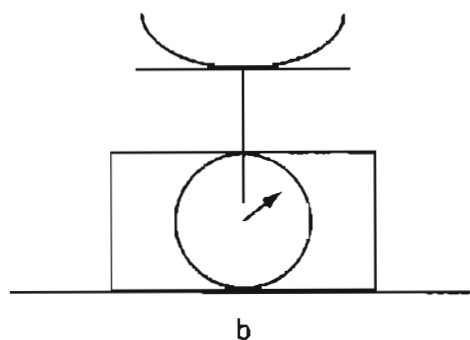
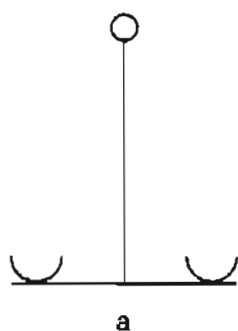
***1.6** A technical publication describes a new model 20-hp Stirling (air cycle) engine that drives a 68-kW generator. Is this possible?

****1.7** Your boss announced that the speed of the company Boeing 737 is to be cut from 525 mi/hr to 475 mi/hr to “conserve fuel,” thus cutting consumption from 2200 gal/hr to 2000 gal/hr. How many gallons are saved in a 1000-mi trip?

****1.8** From Parade Magazine, August 31, 1997, page 8 by Marilyn Voss Savant:

Can you help with this problem? Suppose it takes one man 5 hours to paint a house, and it takes another man 3 hours to paint the same house. If the two men work together, how many hours would it take them? This is driving me nuts. Calculate the answer.

***1.9** Two scales are shown, a balance (a) and a spring scale (b)



In the balance calibrated weights are placed in one pan to balance the object to be weighted in the other pan. In the spring scale, the object to be weighted is placed on the pan and a spring is compressed that moves a dial on a scale in kg.

State for each device whether it directly measures mass or weight. Underline your answer. State in *one* sentence for each the reason for your answer.

- *1.10** In the American Engineering system of units, the viscosity can have the units of $(\text{lb}_f)(\text{hr})/\text{ft}^2$, while in a handbook the units are $(\text{g})/(\text{cm})(\text{s})$. Convert a viscosity of $20.0 (\text{g})/(\text{m})(\text{s})$ to the given American Engineering units.
- **1.11** Thermal conductivity in the American Engineering system of units is:

$$k = \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(^\circ\text{F}/\text{ft})}$$

Change this to:

$$\frac{\text{kJ}}{(\text{day})(\text{m}^2)(^\circ\text{C}/\text{cm})}$$

- **1.12** Water is flowing through a 2-inch diameter pipe with a velocity of 3 ft/s.
- (a) What is the kinetic energy of the water in $\frac{(\text{ft})(\text{lb}_f)}{(\text{lb}_m)}$?
- (b) What is the flowrate in gal/min?
- *1.13** The contents of packages are often labeled in a fashion such as “net weight 250 grams.” Is it correct to so label a package?
- *1.14** What is meant by a scale that shows a weight of “21.3 kg”?
- *1.15** A tractor pulls a load with a force equal to 800 lb (4.0 kN) with a velocity of 300 ft/min (1.5 m/s). What is the power required using the given American Engineering system data? The SI data?
- *1.16** What is the kinetic energy of a vehicle with a mass of 2300 kg moving at the rate of 10.0 ft/sec in Btu? 1 Btu = 778.2 (ft)(lb_f).
- *1.17** A pallet of boxes weighing 10 tons is dropped from a lift truck from a height of 10 feet. The maximum velocity the pallet attains before hitting the ground is 6 ft/s. How much kinetic energy does the pallet have in (ft)(lb_f) at this velocity?
- ***1.18** The efficiency of cell growth in a substrate in a biotechnology process was given in a report as

$$\eta = \frac{Y_{x/s}^c \gamma_b \Delta H_b^c / e^-}{\Delta H_{\text{cat}}}$$

In the notation table

η = energetic efficiency of cell metabolism (energy/energy)

$Y_{x/s}^c$ = cell yield, carbon basis (cells produced/substrate consumed)

γ_b = degree of reductance of biomass (available electron equivalents/
g mole carbon, such as 4.24 e⁻equiv./mol cell carbon)

$\Delta H_b^c/e^-$ = biomass heat of combustion (energy/available electron equiv.)

ΔH_{cat}^c = available energy from catabolism (energy/mole substrate carbon)

Is there a missing conversion factor? If so, what would it be? The author claims that the units in the numerator of the equation are (mol cell carbon/mol substrate carbon) (mol available e^- /mol cell carbon) (heat of combustion/mol available e^-). Is this correct?

- *1.19 Leaking oil tanks have become such environmental problems that the Federal Government has implemented a number of rules to reduce the problem. A leak from a small hole in a tank can be predicted from the following relation:

$$Q = 0.615\sqrt{(2\Delta p)/\rho}$$

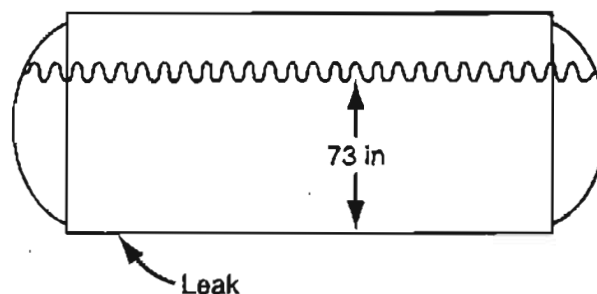
where Q = the leakage rate

S = crosssectional area of the leak

Δp = pressure drop

ρ = fluid density

To test the tank, the vapor space is pressurized with N_2 to a pressure of 23 psig. If the tank is filled with 73 inches of gasoline (sp. gr. = 0.703) and the hole is 1/4 in. in diameter, what is the value of Q (in ft^3/hr)?



- **1.20 In an article on measuring flows from pipes, the author calculated $q = 80.8 \text{ m}^3/\text{s}$ using the formula

$$q = CA_1\sqrt{\frac{2gV(p_1 - p_2)}{1 - (A_1/A_2)^2}}$$

where q = volumetric flow rate, m^3/s

C = dimensionless coefficient, 0.6

A_1 = area, 2 m^2

A_2 = area, 5 m^2

V = specific volume, $10^{-3} \text{ m}^3/\text{kg}$

p = pressure; $p_1 - p_2$ is 50 kPa

g = acceleration of gravity

Was the calculation correct? (Answer Yes or No and explain briefly the reasoning underlying your answer.)

- ***1.21 The density of a certain liquid is given an equation of the following form:

$$\rho = (A + Bt)e^{CP}$$

where ρ = density in g/cm³

t = temperature in °C

P = pressure in atm

- (a) The equation is dimensionally consistent. What are the units of A , B , and C ?
 (b) In the units above,

$$A = 1.096$$

$$B = 0.00086$$

$$C = 0.000953$$

Find A , B , and C if ρ is expressed in lb/ft³, t in °R, and P in lb_f/in.²

- ***1.22 A relation for a dimensionless variable called the compressibility (z) is $z = 1 + \rho B + \rho^2 C + \rho^3 D$ where ρ is the density in g mol/cm³. What are the units of B , C , and D ? Convert the coefficients in the equation for z so that the density can be introduced into the equation in the units of lb_m/ft³ thus: $z = 1 + \rho^* B^* + (\rho^*)^2 C^* + (\rho^*)^3 D^*$ where ρ^* is in lb_m/ft³. Give the units for B^* , C^* , and D^* , and give the equations that relate B^* to B , C^* to C , and D^* to D .

- ***1.23 The velocity in a pipe in turbulent flow is expressed by the following equation

$$u = k \left[\frac{\tau}{\rho} \right]^{1/2}$$

where τ is the shear stress in N/m² at the pipe wall, ρ is the density of the fluid in kg/m³, u is the velocity, and k is a coefficient. You are asked to modify the equation so that the shear stress can be introduced in the units of τ' which are lb_f/ft², and the density be ρ' for which the units are lb_m/ft³ so that the velocity u' comes out in the units of ft/s. Show all calculations, and give the final equation in terms of u' , τ' , and ρ' so a reader will know that American Engineering units are involved in the equation.

- *1.24 Without integrating, select the proper answer for

$$\int \frac{dx}{x^2 + a^2} = \left\{ \begin{array}{lll} a & \arctan & (ax) \\ a & \arctan & (x/a) \\ (1/a) & \arctan & (x/a) \\ (1/a) & \arctan & (ax) \end{array} \right\} + \text{constant}$$

where x = length and a is a constant.

- *1.25 In many plants the analytical instruments are located some distance from the equipment being monitored. Thus, some delay exists before detecting a process change and the activation of an alarm.

In a chemical plant, air samples from a process area are continuously drawn through a 1/4 in. diameter tube to an analytical instrument located 125 ft from the process area. The 1/4 in. tubing has an outside diameter of 0.25 in. (6.35 mm) and a wall thickness of 0.030 in. (0.762 mm). The sampling rate is 10 cm³/sec under ambient conditions of 22°C and 1.0 atm. The pressure drop in the transfer line can be considered negligible. Chlorine gas is used in the process, and if it leaks from the process, it can poison workers who might be in the area of the leak. Determine the time required to detect a leak of chlorine in the process area with the equipment currently installed. You may assume the analytical equipment takes 5 sec to respond once the gas reaches the instrument. You may also assume that samples travel through the instrument sample tubing without dilution by mixing with the air ahead of the sample. Is the time excessive? How might the delay be reduced? (Adapted from Problem 13, in *Safety Health and Loss Prevention in Chemical Processes* published by the American Institute of Chemical Engineers, New York (1990).

- *1.26 In 1916 Nusselt derived a theoretical relation for predicting the coefficient of heat transfer between a pure saturated vapor and a colder surface:

$$h = 0.943 \left(\frac{k^3 \rho^2 g \lambda}{L \mu \Delta T} \right)^{1/4}$$

where h = mean heat transfer coefficient, Btu/(hr) (ft²) (Δ°F)

k = thermal conductivity, Btu/(hr) (ft) (Δ°F)

ρ = density, lb/ft³

g = acceleration of gravity, 4.17 × 10⁸ ft/(hr)²

λ = enthalpy change, Btu/lb

L = length of tube, ft

μ = viscosity, lb_m/(hr) (ft)

ΔT = temperature difference, Δ°F

What are the units of the constant: 0.943?

- *1.27 Explain in detail whether the following equation for flow over a rectangular weir is dimensionally consistent. (This is the modified Francis formula.)

$$q = 0.415 (L - 0.2 h_o) h_o^{1.5} \sqrt{2g}$$

where q = volumetric flow rate, ft³/s

L = crest height, ft

h_o = weir head, ft

g = acceleration of gravity, 32.2 ft/(s)²

- *1.28 A useful dimensionless number called the *Reynolds number* is $\frac{DU\rho}{\mu}$

where D = diameter or length

U = some characteristic velocity

ρ = fluid density

μ = fluid viscosity

Calculate the Reynolds number for the following cases:

	1	2	3	4
D	2 in.	20 ft	1 ft	2 mm
U	10 ft/s	10 mi/hr	1 m/s	3 cm/s
ρ	62.4 lb/ft ³	1 lb/ft ³	12.5 kg/m ³	25 lb/ft ³
μ	0.3 lb _m /(hr)(ft)	0.14×10^{-4} lb _m /(s)(ft)	2×10^{-6} centipoise (cp)	1×10^{-6} centipoise

- ***1.29** Computers are used extensively in automatic plant process control systems. The computers must convert signals from devices monitoring the process, evaluate the data using the programmed engineering equations, and then feed back the appropriate control adjustments. The equations must be dimensionally consistent. Therefore, a conversion factor must be part of the equation to change the measured field variable into the proper units. Crude oil pumped from a storage unit to a tanker is to be expressed in tons/hr, but the field variables of density and the volumetric flow rate are measured in lb/ft³ and gal/min, respectively. Determine the units and the numerical values of the factors necessary to convert the field variables to the desired output.
- *1.30** If you subtract 1191 cm from 1201 cm, each number with four significant figures, does the answer of 10 cm have two or four (10.00) significant figures?
- *1.31** What is the sum of
- 3.1472
 32.05
 1234
 8.9426
 0.0032
 9.00
- to the correct number of significant figures?
- *1.32** Suppose you make the following sequence of measurements for the segments in laying out a compressed air line:
- 4.61 m
 210.0 m
 0.500 m
- What should be the reported total length of the air line?
- *1.33** Given that the width of a rectangular duct is 27.81 cm, and the height is 20.49 cm, what is the area of the duct with the proper number of significant figures?
- *1.34** Multiply 762 by 6.3 to get 4800.60 on your calculator. How many significant figures exist in the product, and what should the rounded answer be?
- *1.35** Suppose you multiply 3.84 times 0.36 to get 1.3824. Evaluate the maximum relative error in (a) each number and (b) the product. If you add the relative errors in the two numbers, is the sum the same as the relative error in their product?

***1.36** A problem was posed as follows:

The equation for the velocity of a fluid stream measured with a Pitot tube is

$$v = \sqrt{\frac{2\Delta p}{\rho}}$$

where v = velocity

Δp = pressure drop

ρ = density of fluid

If the pressure drop is 15 mm Hg, and the density of the fluid is 1.20 g/cm³, calculate the velocity in ft/s. The solution given was

$$\begin{aligned} & \frac{2}{1} \left| \frac{15 \text{ mmHg}}{760 \text{ mm Hg}} \right| \left| \frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ Pa}} \right| \left| \frac{\frac{1 \text{ N}}{\text{m}^2}}{(1 \text{ N})(\text{s}^2)} \right| \left| \frac{10^5 (\text{g})(\text{cm})}{1.20 \text{ g}} \right| \left| \frac{(\text{cm}^3)}{\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2} \right| \\ &= \left[\frac{33322.4 \text{ cm}^2}{\text{s}^2} \right]^{1/2} = 182.5 \frac{\text{cm}}{\text{s}} \end{aligned}$$

Check that the answer is correct by

- Repeating the calculations but carrying them out in reverse order starting with the answer.
 - Consolidating the units and making sure the final set of units are correct.
 - Repeating the calculations with a pressure drop of 30 mm Hg and a fluid density of 1 g/cm³, and determining if the answer has changed in the correct proportionality.
 - Reviewing the calculation procedure and determining if the powers have been calculated correctly and the conversion factors are correct and not inverted.
- *1.37** Repeat Problem 1.36 for the solutions in (a) Example 1.2, (b) Example 1.3, (c) Example 1.4, and (d) Example 1.5.
- *1.38** The dimensionless growth factor of a cell $Y_{X/S}^c$ can be represented by an input-output relation for cell growth:

$$Y_{X/S}^c = \frac{G_{\text{ATP}} Y_{X/\text{ATP}}}{1 + G_{\text{ATP}} Y_{X/\text{ATP}}}$$

where

G_{ATP} = mol ATP produced/mol carbon catabolized (utilized)

$Y_{X/\text{ATP}}$ = mole substrate carbon/mol ATP

$Y_{X/S}^c$ = dimensionless stoichiometric coefficient associated with the biomass produced in the reaction

ATP stands for the adenosine triphosphate that is involved in the catabolism.

Calculate the growth factor for the anerobic fermentation of glucose ($C_6H_{12}O_6$) to ethanol with the N supplied by NH_3 to form cells with the formula $CH_{1.75}O_{0.38}N_{0.25}$. Experiments show that $Y_{X/ATP} = 0.404$ mol cell C/mol ATP. The literature shows that 2 moles of ATP are synthesized per mole of glucose catabolized.

***1.39** Calculate the protein elongation (formation) rate per mRNA per minute based on the following data:

- (a) One protein molecule is produced from x amino acid molecules.
- (b) The protein (polypeptide) chain elongation rate per active ribosome uses about 1200 amino acids/min
- (c) One active ribosome is equivalent to 264 ribonucleotides.
- (d) $3x$ ribonucleotides equal each mRNA.

Messenger RNA (mRNA) is a copy of the information carried by a gene in DNA, and is involved in protein synthesis.

CHAPTER 2

MOLES, DENSITY, AND CONCENTRATION

2.1 The Mole	43
2.2 Density	48
2.3 Specific Gravity	51
2.4 Flow Rate	56
2.5 Mole Fraction and Mass (Weight) Fraction	57
2.6 Analyses of Multicomponent Solutions and Mixtures	59
2.7 Concentration	62

Your objectives in studying this chapter are to be able to:

1. Define a kilogram mole, pound mole, and gram mole.
2. Convert from moles to mass and vice versa for any chemical compound given the molecular weight.
3. Calculate the molecular weight from the molecular formula.
4. Define density and specific gravity.
5. Calculate the density of a liquid or solid given its specific gravity and the vice versa.
6. Look up and interpret the meaning of density and specific gravity of a liquid or solid in reference tables.
7. Specify the common reference material(s) used to determine the specific gravity of liquids and solids.
8. Convert the composition of a mixture from mole fraction (or percent) to mass (weight) fraction (or percent) and vice versa.
9. Transform a material from one measure of concentration to another, including mass/volume, moles/volume, ppm, and molarity.
10. Calculate the mass or number of moles of each component in a mixture given the percent (or fraction) composition, and vice versa, and compute the pseudo-average molecular weight.
11. Convert a composition given in mass (weight) percent to mole percent, and vice versa.

In this chapter we review a number of concepts, terms, and procedures with which you are no doubt somewhat familiar. We believe a firm grasp of this material is essential to the proper implementation of material and energy balance calculations. If you make sure that you have a sound command of this material, you will reduce the number of errors that you will make when formulating material and energy balances throughout the remainder of the text.

Looking Ahead

In this chapter we first discuss the mole. Then we review some of the common conventions used in reporting physical properties, including density, specific gravity, measures of concentration, and flow rates.

2.1 The Mole

What is a mole? For our purposes we say that a **mole** is a certain amount of material corresponding to a specified number of molecules, atoms, electrons, or any other specified types of particles.

The word *mole* appears to have been introduced by William Ostwald in 1896, who took it from the Latin word *moles* meaning "heap" or "pile." If you think of a mole as a large heap of particles, you will have the general idea. A more precise definition was set out by the 1969 International Committee on Weights and Measures, which approved the mole (symbol mol in the SI system) as being "the amount of a substance that contains as many elementary entities (6.022×10^{23}) as there are atoms in 0.012 kg of carbon 12." The entities may be atoms, molecules, ions, or other particles. Thus, you could have a mole of eggs consisting of 6.022×10^{23} eggs! If you had data amounting to 1 mol of bytes on your computer hard disk, how many gigabytes of space would be filled? It would be more than 6×10^{14} gigabytes!

In the SI system a mole is composed of 6.022×10^{23} (Avogadro's Number) molecules. However, for convenience in calculations and for clarity, we will make use of other specifications for moles such as the **pound mole** (lb mol, comprised of $6.022 \times 10^{23} \times 453.6$) molecules, the kg mol (kilomole, kmol, comprised of 1,000 moles), and so on. You will find that such nonconforming (to SI) definitions of the amount of material will help avoid excess details in many calculations. To keep the units straight, we will use the designation of g mol for the SI mole. What would a ton mole of molecules consist of?

One important calculation you should become skilled at is to convert the number of moles to mass and the mass to moles. To do this you make use of the **molecular weight**—the mass per mole:

$$\text{molecular weight (MW)} = \frac{\text{mass}}{\text{mole}}$$

Thus, the calculations you carry out are

$$\text{the g mol} = \frac{\text{mass in g}}{\text{molecular weight}}$$

$$\text{the lb mol} = \frac{\text{mass in lb}}{\text{molecular weight}}$$

and

$$\text{mass in g} = (\text{MW})(\text{g mol})$$

$$\text{mass in lb} = (\text{MW})(\text{lb mol})$$

For example

$$\frac{100.0 \text{ g H}_2\text{O}}{1} \left| \frac{1 \text{ g mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right| = 5.56 \text{ g mol H}_2\text{O}$$

$$\frac{6.0 \text{ lb mol O}_2}{1} \left| \frac{32.0 \text{ lb O}_2}{1 \text{ lb mol O}_2} \right| = 192 \text{ lb O}_2$$

Values of the molecular weights (relative molar masses) are built up from the tables of atomic weights based on an arbitrary scale of the relative masses of the elements. The **atomic weight** of an element is the mass of an atom based on the scale that assigns a mass of exactly 12 to the carbon isotope ^{12}C . The terms atomic “weight” and molecular “weight” are universally used by chemists and engineers instead of the more accurate terms atomic “mass” and molecular “mass.” Since weighting was the original method for determining the comparative atomic masses, as long as they were calculated in a common gravitational field, the relative values obtained for the atomic “weights” were identical with those of the atomic “masses.”

Appendix B lists the atomic weights of the elements. On this scale of atomic weights, hydrogen is 1.008, carbon is 12.01, and so on. (In most of our calculations we shall round these off to 1 and 12, respectively, for convenience.)

A **compound** is composed of more than one atom, and the molecular weight of the compound is nothing more than the sum of the weights of atoms of which it is composed. Thus H_2O consists of 2 hydrogen atoms and 1 oxygen atom, and the molecular weight of water is $(2)(1.008) + 16.000 = 18.02$. These weights are all relative to the ^{12}C atom being 12.0000, and you can attach any unit of mass you desire to these weights; for example, H_2 can be 2.016 g/g mol, 2.016 lb/lb mol, 2.016 ton/ton mol, and so on. Appendices D, E, and F and the CD in the back of this book list molecular weights.

You can compute the average molecular weight of a mixture even though its components are not chemically bonded if the composition of the mixture is known. Later in Section 2.7 we show how to calculate the fictitious quantity called the aver-

age molecular weight of air. Of course, for a material such as fuel oil or coal, whose composition may not be exactly known, you cannot determine an exact molecular weight, although you might estimate an approximate average molecular weight good enough for engineering calculations. *Keep in mind that the symbol lb without any subscript in this book refers to lb_m unless otherwise stated.*

EXAMPLE 2.1 Calculation of Molecular Weight

Since the discovery of superconductivity almost 100 years ago, scientists and engineers have speculated about how it can be used to improve the use of energy. Until recently most applications were not economically viable because the niobium alloys used had to be cooled below 23K by liquid He. However, in 1987 superconductivity in Y-Ba-Cu-O material was achieved at 90 K, a situation that permits the use of less expensive liquid N_2 cooling.

What is the molecular weight of the following cell of a superconductor material? (The figure represents one cell of a larger structure.)

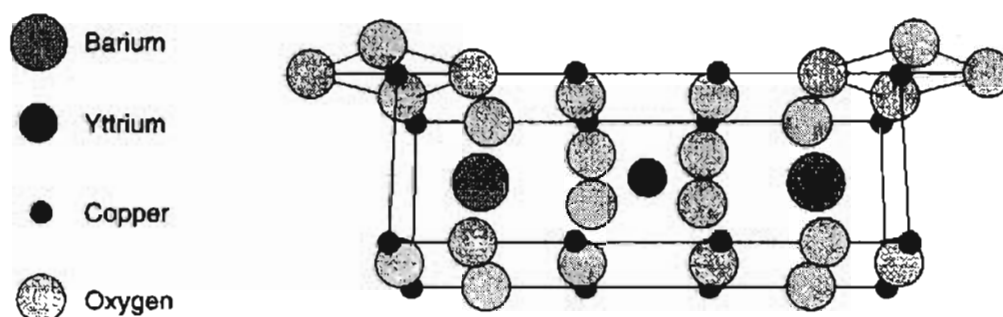


Figure E2.1

Solution

You can count the number of atoms of each element by examining Figure E2.1. Look up the atomic weights of the elements from the table in Appendix B. Assume that one cell is a molecule. By counting the atoms and carrying out the brief calculations below, you obtain the molecular weight of the cell.

Element	Number of atoms	Atomic weights	Mass (g)
Ba	2	137.34	2(137.34)
Cu	16	63.546	16(63.546)
O	24	16.00	24(16.00)
Y	1	88.905	1(88.905)
Total			1764.3

The molecular weight of the cell is 1764.3 atomic masses/1 molecule, or 1764.3 g/g mol.

Finally, check your calculations.

EXAMPLE 2.2 Use of Molecular Weights to Convert Mass to Moles

If a bucket holds 2.00 lb of NaOH, how many

- (a) Pound moles of NaOH does it contain?
 (b) Gram moles of NaOH does it contain?

Solution

You want to convert pounds to pound moles, and then convert respective values to the SI system of units.

Look up the molecular weight of NaOH, or calculate it from the atomic weights. It is 40.0.

$$(a) \frac{2.00 \text{ lb NaOH}}{1} \left| \frac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right| = 0.050 \text{ lb mol NaOH}$$

$$(b_1) \frac{2.00 \text{ lb NaOH}}{1} \left| \frac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right| \left| \frac{454 \text{ g mol}}{1 \text{ lb mol}} \right| = 22.7 \text{ g mol}$$

$$(b_2) \frac{2.00 \text{ lb NaOH}}{1} \left| \frac{454 \text{ g}}{1 \text{ lb}} \right| \left| \frac{1 \text{ g mol NaOH}}{40.0 \text{ g NaOH}} \right| = 22.7 \text{ g mol}$$

Check your answer. Convert the 2.00 lb of NaOH to the SI system first, and then make the calculation.

EXAMPLE 2.3 Use of Molecular Weights to Convert Moles to Mass

How many pounds of NaOH are in 7.50 g mol of NaOH?

Solution

The problem concerns converting g mol to lb.

From Example 2.2, the MW of NaOH is 40.0.

Basis: 7.50 g mol of NaOH

$$\frac{7.50 \text{ g mol NaOH}}{1} \left| \frac{1 \text{ lb mol}}{454 \text{ g mol}} \right| \left| \frac{40.0 \text{ lb NaOH}}{1 \text{ lb mol NaOH}} \right| = 0.661 \text{ lb NaOH}$$

Note the conversion between lb mol and g mol converts the value of 7.50 g mol from the SI to the AE system of units. Could you first convert 7.50 g mol NaOH to g of NaOH, and then use the conversion of 454 g = 1 lb to get lb NaOH? Of course.

SELF-ASSESSMENT TEST

Questions

1. Answer the following questions true or false:
 - a. The pound mole is comprised of 2.73×10^{26} molecules
 - b. The kilogram mole is comprised of 6.022×10^{26} molecules.
 - c. Molecular weight is the mass of a compound or element per mole.
2. What is the molecular weight of acetic acid (CH_3COOH)?

Problems

1. Convert the following:
 - a. 120 g mol of NaCl to g.
 - b. 120 g of NaCl to g mol.
 - c. 120 lb mol of NaCl to lb.
 - d. 120 lb of NaCl to lb mol.
2. Convert 39.8 kg of NaCl per 100 kg of water to kg mol of NaCl per kg mol of water.
3. How many lb mol of NaNO_3 are there in 100 lb?

Thought Problem

1. There is twice as much copper in 480 g of copper as there is in 240 g of copper, but is there twice as much copper in 480 g of copper as there is silver in 240 g of silver?
2. If a mole of doughnuts contains 6.022×10^{23} doughnuts, can you also say that the mole of doughnuts contains the same number of moles of doughnut holes when holes are not doughnut material?

Discussion Problems

1. In the journal *Physics Education* (July 1977, p. 276) McGlashan suggested that the physical quantity we call the mole is not necessary. Instead, it would be quite feasible to use molecular quantities, that is, number of molecules or atoms, directly. Instead of $pV = nRT$ where n denotes the number of moles of a substance, we should write $pV = NkT$ where N denotes the number of molecules and k is the Boltzmann constant [$1.380 \times 10^{-23} \text{J}/(\text{molecule})(\text{K})$]. Thus, for example, $3.0 \times 10^{-29} \text{m}^3/\text{molecule}$ would be the molecular volume for water, a value used instead of $18 \text{cm}^3/\text{g mol}$. Is the proposal a reasonable idea?
2. In asking the question "what is meant by a mole," the following answers were obtained. Explain which are correct and which are not, and why.
 - a. A mole is the molecular weight expressed in grams.
 - b. A mole is the quantity of material in one gram.
 - c. A mole is a certain number of cm^3 of one substance or another.
 - d. A mole is the weight of a molecule expressed in grams.
 - e. A mole is the number of molecules in one gram of a substance.

2.2 Density

A striking example of quick thinking by an engineer who made use of the concept of density was reported by P. K. N. Paniker in the June 15, 1970, issue of *Chemical Engineering*:

The bottom outlet nozzle of a full lube-oil storage tank kept at a temperature of about 80°C suddenly sprang a gushing leak as the nozzle flange became loose. Because of the high temperature of the oil, it was impossible for anyone to go near the tank and repair the leak to prevent further loss.

After a moment of anxiety, we noticed that the engineer in charge rushed to his office to summon fire department personnel and instruct them to run a hose from the nearest fire hydrant to the top of the storage tank. Within minutes, what gushed out from the leak was hot water instead of valuable oil. Some time later, as the entering cold water lowered the oil temperature, it was possible to make repairs.

Density is the ratio of mass per unit volume, as for example, kg/m³ or lb/ft³. Density has both a numerical value and units. To determine the density of a substance, you must find both its volume and its mass. Densities for liquids and solids do not change significantly at ordinary conditions with pressure, but they do change with temperature, as shown in Figure 2.1. Usually we will ignore the effect of temperature on liquid density. **Specific volume** is the inverse of density, such as cm³/g or ft³/lb.

What can you do with density? You use it to determine the volume of a given mass, or the mass of a given volume of material. For a compound

$$\rho = \text{density} = \frac{\text{mass}}{\text{volume}} = \frac{m}{V}$$

$$\hat{V} = \text{specific volume} = \frac{\text{volume}}{\text{mass}} = \frac{V}{m}$$

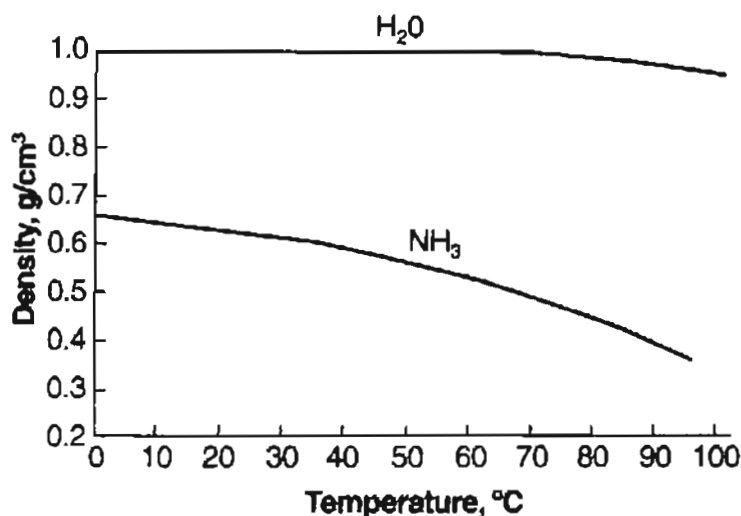


Figure 2.1 Densities of liquid H₂O and NH₃ as a function of temperature.

so that given the density of the compound you can calculate the volume of a given mass. For example, given that the density of *n*-propyl alcohol is 0.804 g/cm³, what would be the volume of 90.0 g of the alcohol? The calculation is

$$\frac{90.0 \text{ g}}{0.804 \text{ g}} \left| \frac{1 \text{ cm}^3}{1 \text{ g}} \right| = 112 \text{ cm}^3$$

Some quantities related to density are molar density (ρ/MW) and molar volume (MW/ρ). By analogy, in a packed bed of solid particles containing void spaces, the bulk density is

$$\rho_B = \text{bulk density} = \frac{\text{total mass of solids}}{\text{total empty bed volume}}$$

A homogeneous mixture of two or more components, whether solid, liquid, or gaseous, is called a **solution**. Solutions have variable composition while pure substances do not. That is, the relative amounts of the various components in a solution can vary. Thus, air, salt water, and 16-carat gold each are solutions. For some solutions, to calculate the density of the solution, you can make a linear combination of the individual components by adding the respective masses and volumes, and then dividing:

$$V = \sum_{i=1}^n V_i \quad \text{where } n = \text{number of components}$$

$$m = \sum_{i=1}^n m_i$$

$$\rho_{\text{solution}} = \frac{m}{V}$$

For others you cannot. Examine Figure 2.2.

SELF-ASSESSMENT TEST

Questions

- For numbers such as 2 mL of water + 2 mL of ethanol, does the sum equal to 4 mL of the solution?
- Answer the following questions true or false:
 - The inverse of the density is the specific volume.
 - Density of a substance is the mass per unit volume.
 - The density of water is less than the density of mercury.

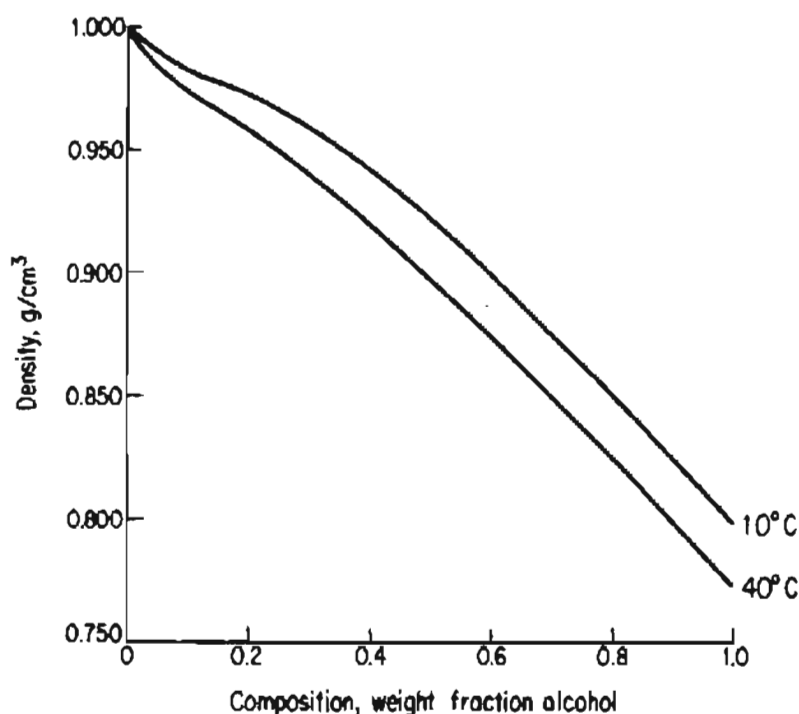


Figure 2.2 Density of a mixture of ethyl alcohol and water as a function of composition.

3. A cubic centimeter of mercury has a mass of 13.6 g at Earth's surface. What is the density of mercury?
4. What is the approximate density of water at room temperature in kg/m^3 ?

Problems

1. The density of a material is 2 kg/m^3 . What is its specific volume?
2. An empty 10 gal tank weighs 4.5 lb. What is the total weight of the tank plus the water when it is filled with 5 gal of water?
3. If you add 50 g of sugar to 500 mL of water, how do you calculate the density of the sugar solution?

Thought Problems

1. The representative of Lloyd's Register of Shipping testified in a Houston District court relative to the fraud trial of a Houston businessman. The indictment alleged that the businessman stole 200,000 tons of oil from the Italian owner by delivering the oil to South Africa, and then scuttling the tanker to cover up the theft. The prosecutor asked the insurance representative whether the tanker could have been sunk with a full load of oil. What do you think?
2. A letter to the editor said:

My hobby is photography. I was using a gallon milk container to measure the water needed to dissolve some developer, and realized that the container was about 3 ounces short of a full gallon of liquid when filled to the brim. Is there too much air in the water? I

was taking it directly from the tap, and perhaps should have let the air bubbles settle out. I think we are getting less milk than we think when we buy milk in these containers.

How would you reply to the author explaining what the cause of his dilemma probably is?

3. A refinery tank that had contained gasoline was used for storing pentane. The tank overflowed even when the level indicator said that it was only 85% full. The level indicator measured the weight of fluid. Can you explain what went wrong?

Discussion Problem

1. From *Chemical and Engineering News*, October 12, 1992, p. 10:

Two Dutch scientists have won government and industry support to explore the possibility of raising the level of the ground in coastal areas of their low-lying country by converting subsurface limestone to gypsum with waste sulfuric acid.

The scheme centers on the fact that gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, occupies twice the volume of a corresponding amount of calcium carbonate. The project envisions drilling holes as deep as 1 km at selected sites above limestone strata for injecting the acid. The resulting gypsum should raise the surface as much as several meters. Instances of ground swelling have already occurred from sulfuric acid spillage in the Netherlands at Pernis, an industrial region near Rotterdam.

What do you think of the feasibility of this idea?

2.3 Specific Gravity

In the winter you should have antifreeze in your car radiator. The service station attendant checks the concentration of antifreeze by measuring the specific gravity and, in effect, the density of the thoroughly mixed radiator solution, with a hydrometer. The hydrometer kit contains a small thermometer to enable the attendant to adjust the hydrometer reading to the correct density.

Specific gravity is commonly thought of as a dimensionless ratio. Actually, it should be considered as the ratio of two densities—that of the substance of interest, A , to that of a reference substance—each of which has associated units. In symbols:

$$\text{sp. gr. of } A = \text{specific gravity of } A = \frac{(\text{g/cm}^3)_A}{(\text{g/cm}^3)_{\text{ref}}} = \frac{(\text{kg/m}^3)_A}{(\text{kg/m}^3)_{\text{ref}}} = \frac{(\text{lb/ft}^3)_A}{(\text{lb/ft}^3)_{\text{ref}}}$$

The reference substance for liquids and solids normally is water. Thus, the specific gravity is the ratio of the density of the substance in question to the density of water, which is 1.000 g/cm^3 , 1000 kg/m^3 , or 62.43 lb/ft^3 at 4°C . The specific gravity of gases frequently is referred to air, but may be referred to other gases. We will explain what to do in Chapter 13.

To be precise, when referring to specific gravity, the data should be accompanied by both the temperature of the substance of interest and the temperature at which the reference density is measured. Thus, for solids and liquids the notation

$$\text{sp.gr.} = 0.73 \frac{20^\circ}{4^\circ}$$

can be interpreted as follows: the specific gravity when the solution is at 20°C and the reference substance (implicitly water) is at 4°C is 0.73. In case the temperatures for which the specific gravity is stated are unknown, assume ambient temperature for the substance and 4°C for the water. Since the density of water at 4°C is very close to 1.0000 g/cm^3 , in the SI system the numerical values of the specific gravity and density are essentially equal. The calculations for dibromopentane (DBP), $\text{sp.gr.} = 1.57$, are

$$(a) \quad \frac{1.57 \frac{\text{g DBP}}{\text{cm}^3}}{1.00 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \left| \frac{1.00 \frac{\text{g H}_2\text{O}}{\text{cm}^3}}{\text{cm}^3} \right| = 1.57 \frac{\text{g DBP}}{\text{cm}^3}$$

$$(b) \quad \frac{1.57 \frac{\text{lb DBP}}{\text{ft}^3}}{1.00 \frac{\text{lb H}_2\text{O}}{\text{ft}^3}} \left| \frac{62.4 \frac{\text{lb H}_2\text{O}}{\text{ft}^3}}{\text{ft}^3} \right| = 97.97 \frac{\text{lb DBP}}{\text{ft}^3}$$

$$(c) \quad \frac{1.57 \frac{\text{g DBP}}{\text{cm}^3}}{\text{cm}^3} \left| \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 \right| \frac{1 \text{ kg}}{1000 \text{ g}} = 1.57 \times 10^3 \frac{\text{kg DBP}}{\text{m}^3}$$

or

$$\frac{1.57 \frac{\text{kg DBP}}{\text{m}^3}}{1.00 \frac{\text{kg H}_2\text{O}}{\text{m}^3}} \left| \frac{1.00 \times 10^3 \text{ kg H}_2\text{O}}{\text{m}^3} \right| = 1.57 \times 10^3 \frac{\text{kg DBP}}{\text{m}^3}$$

Note how the units of specific gravity are used here to clarify the calculations, and that the calculation in (a) can be done in your head.

Since densities in the AE system are expressed in lb/ft^3 , and the density of water is about 62.4 lb/ft^3 , you can see that the specific gravity and density values are not numerically equal in the American Engineering system. Yaws, Yang, Hopper,

and Cawley (1991)* is a source for values of liquid densities, and the software on the CD in the back of this book contains portions of Yaw's database.

EXAMPLE 2.4 Calculation of Density Given the Specific Gravity

If a 70% (by weight) solution of glycerol has a specific gravity of 1.184 at 15°C, what is the density of the solution in (a) g/cm³? (b) lb_m/ft³? and (c) kg/m³?

Solution

Use the specific gravity to get density via a reference substance. No temperatures are cited for the reference compound (presumed to be water), hence for simplicity we assume that the temperatures of the water is 4°C, and that water has a density of $1.00 \times 10^3 \text{ kg/m}^3$ (1.00 g/cm^3). The answers are:

- (a) $1.184 \text{ g solution/cm}^3$ (calculated in your head)
- (b) $(1.184 \text{ lb glycerol/ft}^3)/(1 \text{ lb water/ft}^3) \times (62.4 \text{ lb water/ft}^3) = 73.9 \text{ lb solution/ft}^3$
- (c) $1.184 \times 10^3 \text{ kg solution/m}^3$ (calculated in your head).

You may be acquainted with the fact that in the petroleum industry the specific gravity of petroleum products is often reported in terms of a hydrometer scale called °API. The equation for the API scale is

$$^{\circ}\text{API} = \frac{141.5}{\text{sp.gr.} \frac{60^{\circ}\text{F}}{60^{\circ}\text{F}}} - 131.5 \quad (\text{API gravity}) \quad (2.1)$$

or

$$\text{sp.gr.} \frac{60^{\circ}}{60^{\circ}} = \frac{141.5}{^{\circ}\text{API} + 131.5} \quad (2.2)$$

The volume and therefore the density of petroleum products vary with temperature, and the petroleum industry has established 60°F as the standard temperature for volume and API gravity. The CD in the back of the book contains data for petroleum products. The organization that governs SI units is phasing out the use of °API for densities.

Many other specialized systems of measuring density and specific gravity such as Baume (°Be) and Twaddell (°Tw) exist. You can find information about those measures and relationships among them in the references at the end of this chapter.

*Yaws, C. L., H. C. Yang, J. R. Hopper, and W. A. Cawley. "Equation for Liquid Density," *Hydrocarbon Processing*, pp. 103–106 (January 1991).

EXAMPLE 2.5 Application of Specific Gravity to Calculate Mass and Moles

In the production of a drug having a molecular weight of 192, the exit stream from the reactor flows at a rate of 10.5 L/min. The drug concentration is 41.2% (in water), and the specific gravity of the solution is 1.024. Calculate the concentration of the drug (in kg/L) in the exit stream, and the flow rate of the drug in kg mol/min.

Solution

Read the problem carefully because this example is more complicated than the previous examples. You have a solution with some known properties including sp.gr. The strategy for the solution is to use the specific gravity to get the density from which you can calculate the moles per unit volume.

After reading the problem, to make the requirements of the problem clearer, you should draw a picture, and put the given data on the picture. For the first part of the problem, you want to transform the mass fraction of 0.412 into mass per liter of the drug. Take 1.000 kg of the exit solution as a basis for convenience.

Basis: 1.000 kg solution

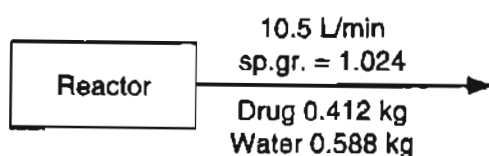


Figure E2.5

How do you get mass per volume (the density) from the given data, which is in terms of mass of drug per mass of solution (41.2%)? Use the specific gravity of the solution. Calculate the density as follows

$$\text{density of solution} = \frac{1.024 \frac{\text{g soln}}{\text{cm}^3}}{1.000 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \left| \frac{1.000 \frac{\text{g H}_2\text{O}}{\text{cm}^3}}{1.000 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \right| = 1.024 \frac{\text{g soln}}{\text{cm}^3}$$

Next convert the amount of drug in 1.000 kg of solution to mass of drug per volume of solution using the density

$$\frac{0.412 \text{ kg drug}}{1.000 \text{ kg soln}} \left| \frac{1.024 \text{ g soln}}{1 \text{ cm}^3} \right| \left| \frac{1 \text{ kg}}{10^3 \text{ g}} \right| \left| \frac{10^3 \text{ cm}^3}{1 \text{ L}} \right| = 0.422 \text{ kg drug/L soln}$$

Could you simplify the last two steps by knowing that 1.000 kg of water is 1.000 L? Certainly.

To get the flow rate, take a different basis, namely 1 minute.

Basis: 1 min \equiv 10.5 L solution

Convert the volume to mass and then to moles using the information previously calculated.

$$\frac{10.5 \text{ L soln}}{1 \text{ min}} \left| \frac{0.422 \text{ kg drug}}{1 \text{ L soln}} \right| \frac{1 \text{ kg mol drug}}{192 \text{ kg drug}} = 0.023 \text{ kg mol/min}$$

How might you check your answers?

Did you notice how we represented a reactor in Figure E2.5 by a simple box with a label? In the interest of simplification (and economy, of course), in this book we usually use a simplified drawing of a process or any equipment that is involved in a discussion or example. Figure 2.3 shows two examples of how you might replace the real apparatus with a sketch. Even Figures 2.3a and 2.3b themselves are simplified drawings of what would look to be very complicated if you took a photograph of the equipment.

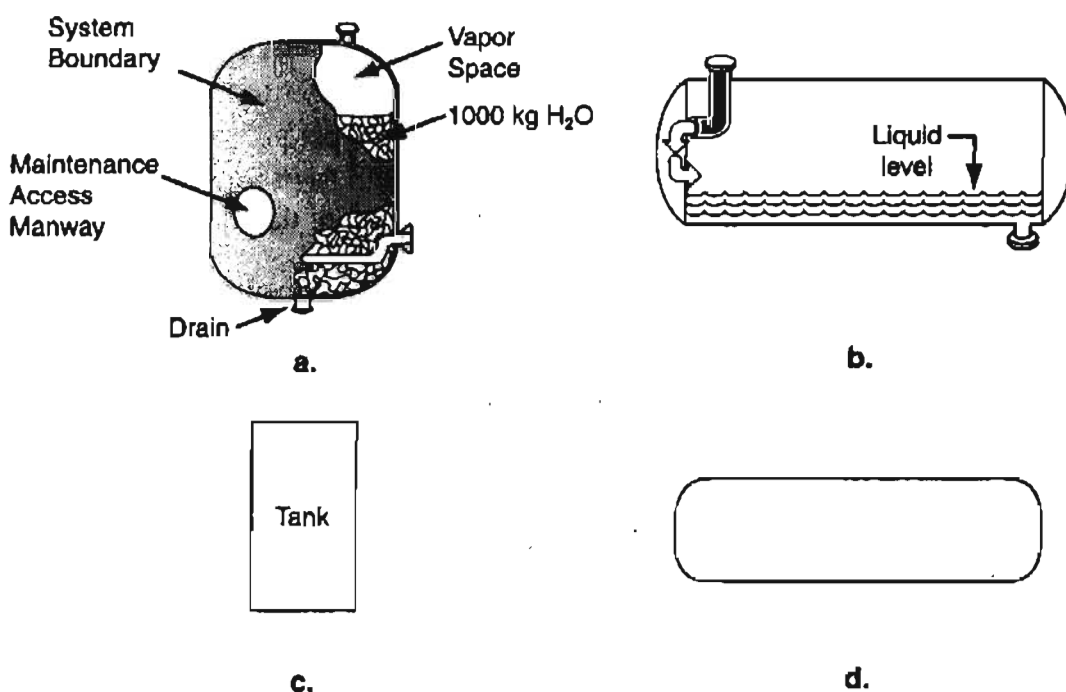


Figure 2.3 Examples of possible substitutes for pictures of equipment by using a simple sketch.

SELF-ASSESSMENT TEST

Questions

- For liquid HCN, a handbook gives: sp. gr. $10^{\circ}\text{C}/4^{\circ}\text{C} = 1.2675$. What does this statement mean?
- Answer the following questions true or false:
 - The density and specific gravity of mercury are the same.

- b. Specific gravity is the ratio of two densities.
- c. If you are given the value of a reference density, you can determine the density of a substance of interest by multiplying by the specific gravity.
- d. The specific gravity is a dimensionless quantity.

Problems

- 1. For ethanol, a handbook gives: sp. gr. $60^{\circ}\text{F} = 0.79389$. What is the density of ethanol at 60°F ?
- 2. The specific gravity of steel is 7.9. What is the volume in cubic feet of a steel ingot weighing 4000 lb?
- 3. The specific gravity of a solution is 0.80 at 70°F . How many cubic feet will be occupied by 100 lb of the solution at 70°F ?
- 4. A solution in water contains 1.704 kg of $\text{HNO}_3/\text{kg H}_2\text{O}$, and the solution has a specific gravity of 1.382 at 20°C . What is the mass of HNO_3 in kg per cubic meter of solution at 20°C ?

Thought Problem

- 1. The National Museum is considering buying a Maya plaque from Honduras that the seller claims to be jade. Jade is either jadite (sp. gr. 3.2 to 3.4) or nephrite (sp. gr. 3.0). What liquids would you recommend using to test whether or not the mask is jade?

2.4 Flow Rate

For continuous processes the **flow rate** of a process stream is the rate at which material is transported through a pipe. In this book we usually use an overlay dot to denote a rate except for the volumetric flow rate F . The **mass flow rate** (\dot{m}) of a process stream is the mass (m) transported through a line per unit time (t).

$$\dot{m} = \frac{m}{t}$$

The **volumetric flow rate** (F) of a process stream is the volume (V) transported through a line per unit time.

$$F = \frac{V}{t}$$

The **molar flow** (n) rate of a process stream is the number of moles (n) of a substance transported through a line per unit time.

$$\dot{n} = \frac{n}{t}$$

Use any consistent units in your calculation.

SELF-ASSESSMENT TEST**Problems**

1. Forty gal/min of a hydrocarbon fuel having a specific gravity of 0.91 flow into a tank truck with a load limit of 40,000 lb of fuel. How long will it take to fill the tank in the truck?
2. Pure chlorine enters a process. By measurement it is found that 2.4 kg of chlorine pass into the process every 3.1 minutes. Calculate the molar flow rate of the chlorine in kg mol/hr.

2.5 Mole Fraction and Mass (Weight) Fraction

Mole fraction is simply the number of moles of a particular compound in a mixture or solution divided by the total number of moles in the mixture or solution. This definition holds for gases, liquids, and solids. Similarly, the **mass (weight) fraction** is nothing more than the **mass (weight)** of the compound divided by the total mass (weight) of all of the compounds in the mixture or solution. Although the mass fraction is the correct word, by custom ordinary engineering usage employs the term **weight fraction**. Mathematically, these ideas can be expressed as

$$\text{mole fraction of } A = \frac{\text{moles of } A}{\text{total moles}}$$

$$\text{mass (weight) fraction of } A = \frac{\text{mass of } A}{\text{total mass}}$$

Mole percent and mass (weight) percent are the respective fractions times 100.

EXAMPLE 2.6 Conversion between Mass (Weight) Fraction and Mole Fraction

An industrial-strength drain cleaner contains 5.00 kg of water and 5.00 kg of NaOH. What are the mass (weight) fractions and mole fractions of each component in the drain cleaner container?

Solution

You are given the masses so that it is easy to calculate the mass fractions. From these values you can then calculate the desired mole fractions.

A convenient way to carry out the calculations in such conversion problems is to form a table, as shown below. Become skilled at doing so because this type of

problem and its inverse, that is, the conversion of mole fraction to mass fraction, will occur quite frequently. List the components, their masses, and their molecular weights in columns.

Basis: 10.0 kg of total solution

Component	kg	Weight fraction	Mol. Wt.	kg mol	Mole fraction
H ₂ O	5.00	$\frac{5.00}{10.0} = 0.500$	18.0	0.278	$\frac{0.278}{0.403} = 0.69$
NaOH	5.00	$\frac{5.00}{10.00} = 0.500$	40.0	0.125	$\frac{0.125}{0.403} = 0.31$
Total	10.00	1.000		0.403	1.00

The kilogram moles are calculated as follows:

$$\frac{5.00 \text{ kg H}_2\text{O}}{18.0 \text{ kg H}_2\text{O}} \left| \frac{1 \text{ kg mol H}_2\text{O}}{18.0 \text{ kg H}_2\text{O}} \right| = 0.278 \text{ kg mol H}_2\text{O}$$

$$\frac{5.00 \text{ kg NaOH}}{40.0 \text{ kg NaOH}} \left| \frac{1 \text{ kg mol NaOH}}{40.0 \text{ kg NaOH}} \right| = 0.125 \text{ kg mol NaOH}$$

Adding these quantities together gives the total kilogram moles.

EXAMPLE 2.7 Nitrogen Requirements Used for the Growth of Cells

In normal living cells, the nitrogen requirement for the cells is provided from protein metabolism (i.e., consumption of the protein in the cells). When individual cells are commercially grown, $(\text{NH}_4)_2\text{SO}_4$ is usually used as the source of nitrogen. Determine the amount of $(\text{NH}_4)_2\text{SO}_4$ consumed in a fermentation medium in which the final cell concentration is 35 g/L in a 500 L volume of the fermentation medium. Assume that the cells contain 9 wt. % N, and that $(\text{NH}_4)_2\text{SO}_4$ is the only nitrogen source.

Solution

Basis: 500 L solution containing 35 g/L

$$\begin{aligned} & \frac{500 \text{ L}}{1} \left| \frac{35 \text{ g cell}}{\text{L}} \right| \left| \frac{0.09 \text{ g N}}{1 \text{ g cell}} \right| \left| \frac{1 \text{ g mol N}}{14 \text{ g N}} \right| \\ & \times \frac{1 \text{ g mol } (\text{NH}_4)_2\text{SO}_4}{1 \text{ g mol N}} \left| \frac{132 \text{ g } (\text{NH}_4)_2\text{SO}_4}{1 \text{ g mol } (\text{NH}_4)_2\text{SO}_4} \right| = 14,850 \text{ g } (\text{NH}_4)_2\text{SO}_4 \end{aligned}$$

SELF-ASSESSMENT TEST

Problems

1. Commercial sulfuric acid is 98% H_2SO_4 and 2% H_2O . What is the mole ratio of H_2SO_4 to H_2O ?
2. A compound contains 50% sulfur and 50% oxygen by mass. Is the empirical formula of the compound (1) SO , (2) SO_2 , (3) SO_3 , or (4) SO_4 ?
3. How many kg of activated carbon (a substance used in removing trace impurities) must be mixed with 38 kg of sand so that the final mixture is 28% activated carbon?
4. A gas mixture contains 40 lb of O_2 , 25 lb of SO_2 , and 30 lb of SO_3 . What is the composition of the mixture in mole fractions?

Discussion Problem

1. Which of the following kinds of ethanol would you regard as being the purest?
 - a. Ethanol made by fermentation followed by fractional distillation to obtain a product composed of 95% ethanol.
 - b. Ethanol made from 95% ethanol by distillation with a compound that gives as the final result 99.8% ethanol.
 - c. Denatured ethanol ("alcohol").
 - d. Ethanol made from ethene.
 - e. Medical ethanol ("alcohol").

2.6 Analyses of Multicomponent Solutions and Mixtures

Some confusion often exists when you are presented with an analysis of a solution or mixture because you may be uncertain as to whether the numbers presented represent mass (weight) fraction or mole fraction.

In this book, the composition of gases will always be presumed to be given in mole percent or fraction unless specifically stated otherwise.

In this book the composition of liquids and solids will be given by mass (weight) percent or fraction unless otherwise specifically stated, as is the common practice in industry.

As an example, look at Table 2.1 that lists the detailed composition of dry air. Do the values in the column headed "Percent" designate mass or mole percent? They are mole percent.

TABLE 2.1 Composition of Clean, Dry Air near Sea Level

Component	Mole percent	Component	Percent
Nitrogen	78.084	Xenon	0.0000087
Oxygen	20.9476	Ozone	
Argon	0.934	Summer	0-0.000007
Carbon dioxide	0.0350	Winter	0-0.000007
Neon	0.001818	Ammonia	0-trace
Helium	0.000524	Carbon monoxide	0-trace
Methane	0.0002	Iodine	0-0.000001
Krypton	0.000114	Nitrogen dioxide	0-0.000002
Nitrous oxide	0.00005	Sulfur dioxide	0-0.001
Hydrogen	0.00005		

A useful quantity in many calculations is the approximate pseudo-average molecular weight of air, a value that can be calculated based on the assumption that all of the air that is not O_2 is N_2 with a pseudo-molecular weight of 28.2.

Component	Moles = percent	Mol. wt.	Lb or kg	Weight %
O_2	21.0	32	672	23.17
N_2	<u>79.0</u>	28.2	<u>2228</u>	<u>76.83</u>
Total	100		2900	100.00
The average molecular weight is 2900 lb/100 lb mol = 29.0, or 2900 kg/100 kg mol = 29				

What value would you get by carrying out a more accurate calculation, taking into account all of the components in Table 2.1?

Table 2.2 shows the analysis of various compounds. Are the values in the table in mass or mole percent?

TABLE 2.2 Chemical Analyses of Various Wastes by Percent

Material	Raw paper	Charred paper	Tire rubber	Dry sewage sludge	Charred sewage sludge	Charred animal manure	Garbage composite A	Garbage composite B
Moisture	3.8	0.8	0.5	13.6	1.2	0.0	3.4	12.3
Hydrogen*	6.9	3.1	4.3	6.7	1.4	5.4	6.6	7.0
Carbon	45.8	84.9	86.5	28.7	48.6	41.2	57.3	44.4
Nitrogen	—	0.1	—	2.6	3.7	1.5	0.5	0.4
Oxygen*	46.8	8.5	4.6	26.5	—	26.0	22.1	42.1
Sulfur	0.1	0.1	1.2	0.6	—	0.4	0.4	0.2
Ash	0.4	2.5	3.4	34.9	45.7	25.5	10.2	5.9

*The hydrogen and oxygen values reflect that due to both the presence of water and that contained within the moisture-free material.

SELF-ASSESSMENT TEST

Questions

1. A mixture is reported as 15% water and 85% ethanol. Should the percentages be deemed to be by mass, mole, or volume?
2. In a recent EPA inventory of 20 greenhouse gases that are emitted in the U.S., carbon dioxide comprised 5.1 million gigagrams (Gg), which was about 70% of all the U.S. greenhouse gas emissions. Fossil fuel combustion in the electric utility sector contributed to about 34% of all the carbon dioxide emissions, while the transportation, industrial, and residential-commercial sectors accounted for 34%, 21%, and 11% of the total, respectively. Are the last four percents mole percent or mass percent?
3. Answer the following questions true or false:
 - a. In engineering practice the compositions of liquids and solids are usually denoted in weight (mass) fraction or percent.
 - b. In engineering practice the composition of gases is usually denoted in mole fraction or percent.
 - c. A pseudo-average molecular weight can be calculated for a mixture of pure components whether solid, liquid, or gases.

Problems

1. Saccharin, an artificial sweetener that is 3000 times sweeter than sucrose, is composed of 45.90% carbon, 2.73% hydrogen, 26.23% oxygen, 7.65% nitrogen, and 17.49% sulfur. Is the molecular formula of saccharin (a) $C_{14}H_{10}O_6N_2S_2$, (b) $C_5H_7O_3NS$, (c) $C_8H_9O_2NS$, $\sqrt{}$ (d) $C_7H_5O_3NS$?
2. A mixture of gases is analyzed and found to have the following composition:

CO_2	12.0%
CO	6.0%
CH_4	27.3%
H_2	9.9%
N_2	44.8%

How much will 3 lb mol of this gas weigh?

3. A liquefied mixture of n-butane, n-pentane, and n-hexane has the following composition:

n- C_4H_{10}	50%
n- C_5H_{12}	30%
n- C_6H_{14}	20%

For this mixture, calculate:

- a. The weight fraction of each component.
- b. The mole fraction of each component.

- c. The mole percent of each component.
- d. The average molecular weight of the mixture.

2.7 Concentration

Concentration generally refers to the quantity of some substance per unit volume, but other related measures of the amount of material frequently occur, as indicated by some of the terms in the following list of ways to express concentration:

- a. Mass per unit volume (lb of solute/ft³ of solution, g of solute/L, lb of solute/barrel, kg of solute/m³).
- b. Moles per unit volume (lb mol of solute/ft³ of solution, g mol of solute/L, g mol of solute/cm³).
- c. Parts per million (**ppm**); parts per billion (ppb), a method of expressing the concentration of extremely dilute solutions; ppm is equivalent to a mass (weight) fraction for solids and liquids because the total amount of material is of a much higher order of magnitude than the amount of solute; it is a mole fraction for gases. Why?
- d. Parts per million by volume (ppmv) and parts per billion by volume (ppbv)
- e. Other methods of expressing concentration with which you may be familiar are molarity (g mol/L), molality (mole solute/kg solvent), and normality (equivalents/L).

A typical example of the use of some of these measures of concentration is the set of guidelines by which the Environmental Protection Agency defines the extreme levels at which the five most common air pollutants could harm people over stated periods of time.

- a. *Sulfur dioxide*: 365 $\mu\text{g}/\text{m}^3$ averaged over a 24-hr period
- b. *Particulate matter* (10 μm or smaller): 150 $\mu\text{g}/\text{m}^3$ averaged over a 24-hr period
- c. *Carbon monoxide*: 10 mg/m^3 (9 ppm) when averaged over an 8-hr period; 40 mg/m^3 (35 ppm) when averaged over 1 hr
- d. *Nitrogen dioxide*: 100 $\mu\text{g}/\text{m}^3$ averaged over 1 year
- e. *Ozone*: 0.12 ppm measured over 1 hour

Note that the gas concentrations are mostly mass/volume except for the ppm.

In the European Union (EU), all gasoline marketed after January 1, 2000, was to be lead-free. Other components are limited as follows: sulfur, less than 150 mg/kg; benzene, 1 vol. %; and aromatics, 42 vol. %. Sulfur in diesel fuel is limited to 350 mg/kg. By 2005, the maximum sulfur content of both gasoline and diesel will

drop to 50 mg/kg. The aromatics limit for gasoline will be volume percent, and diesel will have an 11 vol. % limit for polyaromatics.

Parts per million is a very small number. One ppm is equivalent to 1 inch in 16 miles, or a 1.0 g needle in a metric ton of hay.

EXAMPLE 2.8 Use of ppm

The current OSHA 8-hour limit for HCN in air is 10.0 ppm. A lethal dose of HCN in air is (from the Merck Index) 300 mg/kg of air at room temperature. How many mg HCN/kg air is 10.0 ppm? What fraction of the lethal dose is 10.0 ppm?

Solution

In this problem you have to convert ppm in a gas (a mole ratio, remember!) to a mass ratio.

Basis: 1 kg mol of the air/HCN mixture

Draw a simple picture. Put the data in the figure.

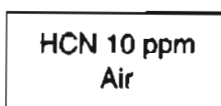


Figure E2.8

You can treat the 10.0 ppm as 10.0 g mol HCN/10⁶ g mol air because the amount of HCN is so small when added to the air in the denominator of the ratio.

$$\text{The 10.0 ppm is } \frac{10.0 \text{ g mol HCN}}{10^6(\text{air} + \text{HCN})\text{g mol}} = \frac{10.0 \text{ g mol HCN}}{10^6 \text{ g mol air}}$$

Next get the MW of HCN so that it can be used to convert moles of HCN to mass of HCN; the MW = 27.03.

Then

$$\begin{aligned} \text{a. } & \frac{10.0 \text{ g mol HCN}}{10^6 \text{ g mol air}} \left| \frac{27.03 \text{ g HCN}}{1 \text{ g mol HCN}} \right| \frac{1 \text{ g mol air}}{29 \text{ g air}} \left| \frac{1000 \text{ mg HCN}}{1 \text{ g HCN}} \right| \\ & \times \frac{1000 \text{ g air}}{1 \text{ kg air}} = 9.32 \text{ mg HCN/kg air} \\ \text{b. } & \frac{9.32}{300} = 0.031 \end{aligned}$$

Does the answer seem reasonable? At least it is not more than 1!

EXAMPLE 2.9 Calculation of Mole Fraction and ppm from a Concentration in g/L

A solution of HNO_3 in water has a specific gravity of 1.10 at 25°C . The concentration of the HNO_3 is 15 g/L of solution. What is the

- Mole fraction of HNO_3 in the solution?
- Ppm of HNO_3 in the solution?

Solution

Let the value of the specific gravity be the value of the density (ignoring any very minor effects related to the density of water).

Basis: 1 L of solution

$$\frac{15 \text{ g HNO}_3}{1 \text{ L soln}} \left| \frac{1 \text{ L}}{1000 \text{ cm}^3} \right| \frac{1 \text{ cm}^3}{1.10 \text{ g soln}} = 0.01364 \frac{\text{g HNO}_3}{\text{g soln}}$$

Basis: 100 g solution

The mass of water in the solution is: $100 - 0.0134 = 99.986 \text{ g H}_2\text{O}$.

	g	MW	g mol	mol fraction
a. HNO_3	0.01364	63.02	2.164×10^{-4}	3.90×10^{-5}
H_2O	99.986	18.016	<u>5.550</u>	<u>1.00</u>
Total			5.550	1.00
b.	$\frac{0.01364}{1} = \frac{13,640}{10^6}$ or 13,640 ppm			

EXAMPLE 2.10 Evaluation of Alternate Processes for the Production of Methyl Methacrylate

Methyl methacrylate can be made using as feed (a) acetone and hydrogen cyanide, or (b) isobutylene. Table E2.10 lists some data assembled from the book by D. T. Allen and D. R. Shonnard (*Green Engineering*, Prentice Hall, Upper Saddle River, N. J., 2002) relating to these two processes. The mass values are on the basis of the production of one pound of methyl methacrylate. Oxygen is also involved but neglected.

TABLE E2.10

Process	Compounds Used	Lb	Value (\$/lb)	TLV* (ppm)	OITF**
(a)	Acetone	0.68	0.43	750	?
	Hydrogen cyanide	0.32	0.67	10	1000
	Methanol	0.37	0.64	200	10
	Sulfuric acid	1.63	0.04	2	10,000
	Methyl methacrylate produced	1.00	0.78	100***	10
(b)	Isobutylene	1.12	0.31	200	?
	Methanol	0.38	0.064	200	10
	Pentane	0.03	0.112	600	?
	Sulfuric acid	0.01	0.04	2	10,000
	Methyl methacrylate produced	1.00	0.78	100***	10

*Threshold limit value for exposure in the workplace by airborne concentrations. Set at a level for which no adverse effects are expected over a worker's lifetime.

**Overall inhalation toxicity factor developed by the U. S. Environmental Protection Agency.

***PEL instead of TLV. PEL is the permissible exposure limit specified by the U. S. Occupational and Safety Administration.

Based on the data in Table E2.10, which process would you recommend be used to produce methyl methacrylate?

Solution

Table E 2.10 includes three different criteria that you can use in the evaluation as well as several compounds involved in each process. The easiest criterion to calculate is the net value of one pound of the product:

$$\begin{aligned}\text{Process(a): Net value} &= 1(\$0.78) - 0.68(\$0.43) - 0.32(\$0.67) \\ &\quad - 0.37(\$0.064) - 1.63(\$0.04) = \$0.18\end{aligned}$$

$$\begin{aligned}\text{Process(b): Net value} &= 1(\$0.78) - 1.12(\$0.31) - 0.38(\$0.64) \\ &\quad - 0.03(\$0.112) - 0.01(\$0.04) = \$0.19\end{aligned}$$

Only a slight difference exists in value.

With respect to the two environmental criteria, a typical procedure is to calculate an index. For TLV, the larger values are of less concern than the smaller ones, hence a mass weighted reciprocals can be used:

$$\text{TLV index} = \sum_i \frac{m_i}{\text{TLV}_i}$$

For OITF, the larger the value, the more concern, hence the index is calculated as:

$$\text{OITF index} = \sum_i (m_i)(\text{OITF})_i$$

For Process (a):

$$\text{TLV index} = \frac{0.68}{750} + \frac{0.32}{10} + \frac{0.37}{200} + \frac{1.63}{2} + \frac{1}{100} = 0.86$$

$$\begin{aligned} \text{OITF index} &= 0.68(?) + 0.32(1000) + 0.37(10) + 1.63(10,000) + 1(10) \\ &\cong 16,600 \end{aligned}$$

For Process (b):

$$\text{TLV index} = \frac{1.12}{200} + \frac{0.38}{200} + \frac{0.03}{600} + \frac{0.01}{2} = 0.01$$

$$\begin{aligned} \text{OITF index} &= 1.12(?) + 0.38(10) + 0.021(?) + 0.01(10,000) + 1(10) \\ &\cong 114 \end{aligned}$$

Other environmental indices can be calculated such as carcinogenicity, persistence in the atmosphere, aquatic persistence, and so on. Capital and operating costs of production also have to be considered in making a decision. However, from the viewpoint of the results of the calculations above, which process would you recommend be used?

SELF-ASSESSMENT TEST

Questions

1. Do parts per million denote a concentration that is a mole ratio?
2. Does the concentration of a component in a mixture depend on the amount of the mixture?
3. Pick the correct answer. How many ppm are there in 1 ppb? (a) 1000, (b) 100, (c) 1, (d) 0.1, (e) 0.01, (f) 0.001?
4. How many ppb are there in 1 ppm?
5. Does 50 ppm represent an increase of five times a value of 10 ppm?
6. Is 10 ppm 400% less than 50 ppm?

Problems

1. How many mg/L is equivalent to a 1.2% solution of a substance in water?
2. If a membrane filter yields a count of 69 fecal coliform (FC) colonies from 5 mL of well water, what should be the reported FC concentration?
3. The danger point in breathing sulfur dioxide for humans is $2620 \mu\text{g}/\text{m}^3$. How many ppm is this value?

Discussion Problems

1. Certain trace elements are known to be toxic to humans but at the same time are essential for your health. For example, would you knowingly drink a glass of water containing 50 ppb of arsenic? The human body normally contains 40 to 300 ppb. Wines contain 5 to 116 ppb of arsenic. Marine fish contain 2,000 to 8,000 ppb. Should you stop eating fish? Another compound essential to humans and animals is selenium. We know that 0.1 to 0.3 ppm of selenium is essential to the diet, but that 5 to 10 ppm is a toxic dose. The Delaney clause of the Food Additives law has been interpreted as prohibiting the presence of any added carcinogen in food. Can selenium be added to your diet via vitamin pills? What about arsenic?
2. It has been suggested that an alternative to using pesticides on plants is to increase the level of natural plant toxins by breeding or gene manipulation. How feasible is this approach from the viewpoint of mutagenic and carcinogenic effects on human beings? For example, solanine and chaconine, some of the natural alkaloids in potatoes, are present at a level of 15,000 μg per 200 g potatoes. This amount is about 1/6 of the toxic level for human beings. Neither alkaloid has been tested for carcinogenicity. The intake of man-made pesticides by humans is estimated at about 150 $\mu\text{g}/\text{day}$. Only about one-half have been shown to be carcinogenic in test animals. The intake of known natural carcinogens is estimated 1 g per day from fruit and vegetables alone omitting coffee (500 μg per cup), bread (185 μg per slice), and cola (2000 $\mu\text{g}/\text{bottle}$).

Prepare a brief report ranking possible carcinogenic hazards from man-made and natural substances. List the possible exposure, source of exposure, carcinogenic dose per person, the relative potency, and risk of death.

Looking Back

We have reviewed the concepts of moles, density, specific gravity, flow rate, mole and mass fraction, and concentration, all of which you probably have previously encountered, but should now be old acquaintances. Become very familiar with using these quantities so that you do not have to puzzle over them when dealing with more advanced subjects.

GLOSSARY OF NEW WORDS

API Scale used to report specific gravity of petroleum compounds.

Average molecular weight A pseudo-molecular weight computed by dividing the mass in a mixture or solution by the number of moles in the mixture or solution.

Atomic weight Mass of an atom based on ^{12}C being exactly 12.

Compound A species composed of more than one element.

Concentration Quantity of a material per unit volume.

Density Mass per unit volume of a compound; molar density is the number of moles divided by the volume.

Flow rate Mass, moles, or volume of a material that is in motion divided by the unit time.

Gram mole 6.022×10^{23} molecules.

Mass fraction Mass of a particular compound in a mixture or solution divided by the total amount of mass present.

Mole Amount of a substance containing 6.022×10^{23} entities.

Mole fraction Moles of a particular compound in a mixture or solution divided by the total number of moles present.

Molecular weight Mass of a compound per mole.

Parts per million Concentration expressed in terms of millionths of units (ppm).

Pound mole $6.022 \times 10^{23} \times 453.6$ molecules.

Solution Homogeneous mixture of two or more compounds.

Specific gravity Ratio of the density of a compound to the density of a reference compound.

Specific volume Inverse of the density (volume per unit mass).

Weight fraction The historical term for mass fraction.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the FAQ in the front material, the following are pertinent.

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9. Winkler, M. A. (ed). *Chemical Engineering Problems in Biotechnology*. Elsevier Science, New York (1990).

Web Sites

<http://chemengineer.about.com>

<http://www.chemistrycoach.com/tutorials-2.html>

<http://www.ex.ac.uk/cimt/dictunit/dictunit.htm>

<http://mcgraw-hill.knovel.com/perrys>

<http://www.retallick.com/resources/netresrc.html>

<http://www.shef.ac.uk/uni/academic/A-C/cpe/mpitt/chemengs.html>

PROBLEMS

- *2.1 The following was a letter to *The Chemical Engineer* (a British publication).

In reply to Dr J. B. Morris in the February issue, of course the symbols g mole and kg mole used to exist, and they still can if you want them to, but not in the SI. Anyway, what is wrong with the mole (mol) and kilomole (kmol)? They are easier both to say and to write. We are all aware of the apparent inconsistency in the choice of the mole rather than the kilomole as the basic SI unit for amount of substance, but the controversy is over now and it is sterile to pursue the matter.

Dr Morris is treading on dangerous ground when he attempts "to remind us that the mole has the dimensions of mass." The mole is certainly related to mass, but this does not confer dimensions of mass on it. The amount of substance is proportional to mass divided by the relative molecular mass, a dimensionless ratio formerly known as the molecular weight. If SI units are involved, a dimensional constant of proportionality numerically equal to 10^3 is normally chosen, but there is no fundamentally compelling reason why we should do so.

Explain what is correct and what is not correct about this letter.

- *2.2 The following objectives were given at the beginning of a chapter discussing the concept of a mole. Do the objectives describe the correct characteristics of the mole? Answer yes or no.

- *Objective 1.* The student will know that the mole is a counting unit and that one mole of any substance contains the same number of units as one mole of any other substance.
 - *Objective 2.* The student will know that the mole is defined as the amount of substance containing Avogadro's number of units or particles of that substance.
 - *Objective 3.* The student will be able to calculate the atomic or molecular masses in grams from the molar masses of the respective atoms or molecules, and vice-versa.
- *2.3** Explain the differences between mole, molecule, and molecular weight.
- *2.4** What is wrong, or correct, about each of the following answers to the question: What is a mole?
- (a) A mole is found in a certain number of cm^3 of one substance or another.
 - (b) A mole is the weight of a molecule expressed in grams.
 - (c) A mole is the number of molecules in one gram of a substance.
 - (d) A mole is the sum of atomic weights.
 - (e) A mole is the molecular weight of an element.
- *2.5** A textbook states: "A mole is a quantity of material whose weight is numerically equal to the molecular weight." State whether this statement is correct, incorrect, or partially correct, and explain in *no more* than three sentences the reasoning behind your answer.
- *2.6** What does the unit mol^{-1} mean? Can a unit be $\text{mol}^{1/3}$?
- *2.7** Select the correct answer(s):
1. A mole of H_2O and a mole of O_2
 - (a) have the same mass
 - (b) contain one molecule each
 - (c) have a mass of 1 g each
 - (d) contain the same number of molecules
 2. One mole of oxygen molecules contains more independent units (O_2) than one mole of oxygen atoms (O).
 - (a) True, because there are two atoms of O for every molecule of O_2 .
 - (b) True, because one mole of O_2 weighs more than one mole of O.
 - (c) False, because both of them have the same number of particles.
 - (d) False, because one mole of O has the same mass as one mole of O_2 .
- *2.8** Calculate the mass of one mole of chlorophyll ($\text{C}_{55}\text{H}_{72}\text{MgN}_4\text{O}_5$)
- *2.9** Convert the following:
- (a) 120 lb moles of NaCl to g.
 - (b) 120 g moles of NaCl to lb.
 - (c) 120 lb of NaCl to g moles.
 - (d) 120 g of NaCl to lb moles.
- *2.10**
- (a) What is the molecular weight of CaCO_3 ?
 - (b) How many g mol are in 10 g of CaCO_3 ?
 - (c) How many lb mol are in 20 lb of CaCO_3 ?
 - (d) How many g are in 2 lb mol of CaCO_3 ?

- *2.11** Convert the following:
- 4 g mol of MgCl_2 to g
 - 2 lb mol of C_3H_8 to g
 - 16 g of N_2 to lb mol
 - 3 lb of $\text{C}_2\text{H}_6\text{O}$ to g mol
- *2.12** How many pounds are there in each of the following
- 16.1 lb mol of pure HCl
 - 19.4 lb mol of KCl
 - 11.9 g mol of NaNO_3
 - 164 g mol of SiO_2
- *2.13** A solid compound was found to contain 42.11% C, 51.46% O, and 6.43% H. Its molecular weight was about 341. What is the formula for the compound?
- *2.14** The structural formulas in Figure P2.14 are for vitamins:
- How many pounds of compound are contained in each of the following (do for each vitamin):
 - 2.00 g mol
 - 16 g
 - How many grams of compound are contained in each of the following (do for each vitamin):
 - 1.00 lb mol
 - 12 lb

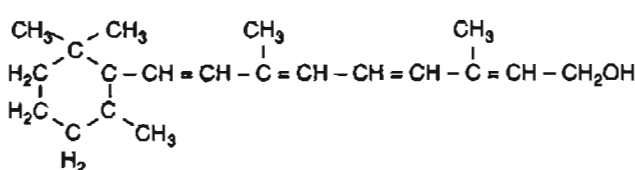
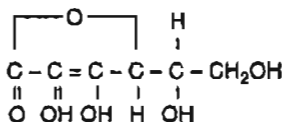
Vitamin	Structural formula	Dietary sources	Deficiency symptoms
Vitamin A	 <p style="text-align: center;">Retinol</p>	Fish liver oils, liver, eggs, fish, butter, cheese, milk; a precursor, β -carotene, is present in green vegetables, carrots, tomatoes, squash	Night blindness, eye inflammation
Ascorbic acid (vitamin C)		Citrus fruit, tomatoes, green peppers, strawberries, potatoes	Scurvy

Figure P2.14

- *2.15** You are asked to decide what size containers to use to ship 1,000 lb of cotton-seed oil of specific gravity equal to 0.926. What would be the minimum size drum expressed in gallons?
- *2.16** The density of a certain solution is 8.80 lb/gal at 80°F. How many cubic feet will be occupied by 10,010 lb of this solution at 80°F?
- *2.17** Which of these three sets of containers represents respectively one mole of lead (Pb), one mol of zinc (Zn), and one mol of carbon (C).

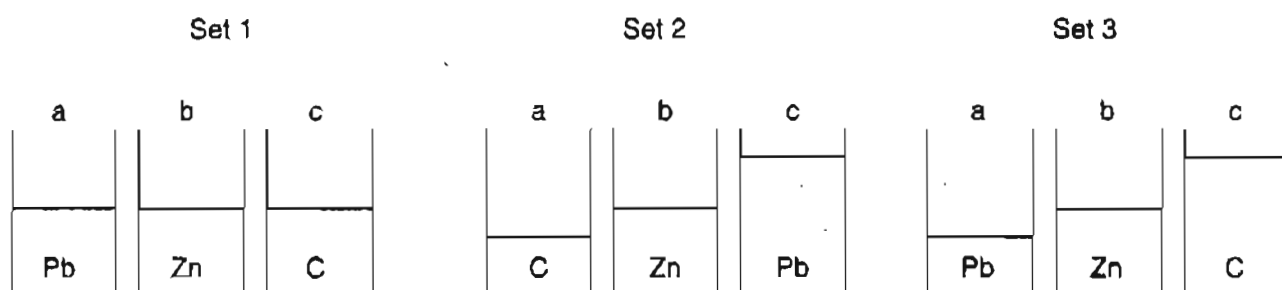


Figure P2.17

***2.18** Inserting genetic material into plant cells to create disease-resistant or herbicide-tolerant strains of crops is now possible with a technique that requires no special equipment. Known as “transformation,” the method differs from microinjection or the ballistic method, which uses a “gun” to fire gold particles coated with the genetic material into cells. Transformation only requires commercially available silicon carbide “whiskers,” a test tube and a mixer. Suppose that 10,000 SiC crystals, with an average diameter of $0.5\ \mu\text{m}$ and length of $20\ \mu\text{m}$, are added to a test tube containing 1,000 plant cells and the genetic material to be inserted. The tube is agitated in a simple mixer for about a minute. Collisions between the cells and needle-like SiC crystals create pores through which the genetic material diffuses into the cell. How many grams of SiC were added? The specific gravity of SiC is 3.17.

****2.19** A cylindrical rod of silica (SiO_2) is heated to its melting point and a thread of silica 0.125 mm in diameter is drawn from the melt. By careful control of the temperature and the tension on the thread being drawn, long fibers of uniform diameter can be obtained that make optical fibers.

- Calculate how much fiber (in km) can be drawn from one cylinder of silica 1.0 m in length and 2.5 cm in diameter. Also estimate the mass. The specific gravity of silica is 2.25.
- Before optical fiber is used, it is typically covered with a thin protective coating of a polymer. The fiber discussed above is coated with a $50\ \mu\text{m}$ layer of a polymer with density $1,740\ \text{kg/m}^3$. How much polymer is needed to coat the entire fiber?

***2.20** In fully vaulted storage systems (see Figure P2.20) the primary container is installed in a completely sealed reinforced concrete vault of monolithic construction. Leak detection is normally achieved by the installation of monitoring wells or sensors in the backfill area. These vaults must be constructed by pouring the floor and walls as continuous structural elements. Chemical resistant coatings on interior surfaces and water barrier coatings on exterior surfaces are required.

If a 10,000 gallon cylindrical tank is to be buried in an approved containment system, the volume of the containment system must by law hold 10% of the volume of the tank. If the void fraction of the backfill material (after compaction) is 20%, what must be the volume in ft^3 of the excavation made before the concrete vault is poured? What is the weight of the backfill if it is sand (density 2.2g/cm^3)?

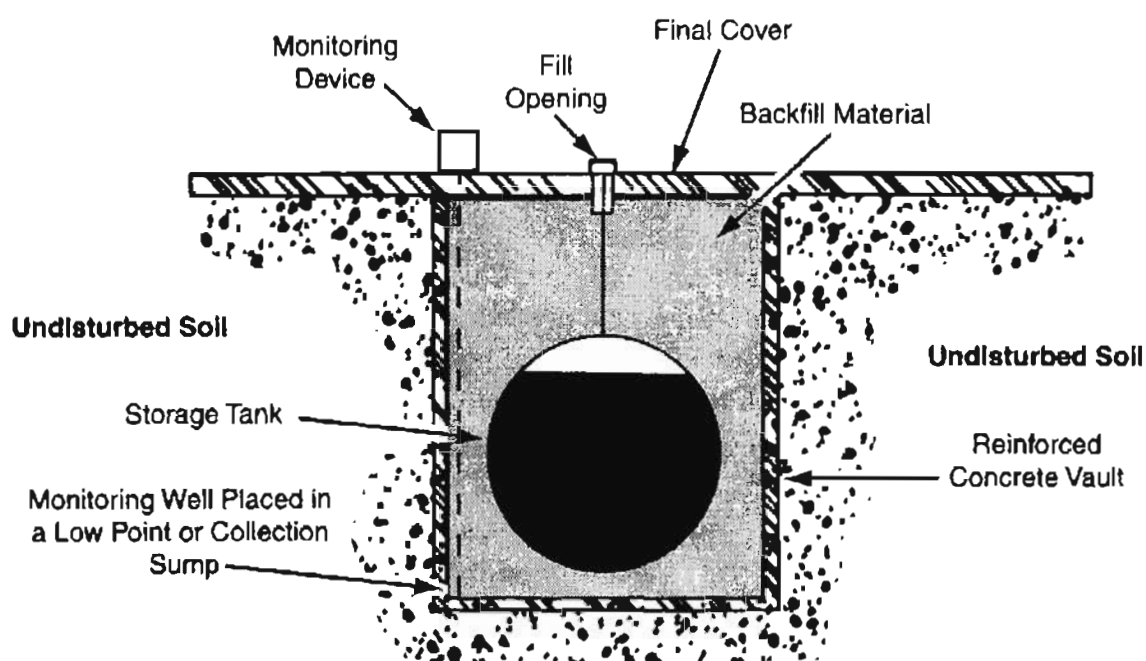


Figure P2.20

- *2.21** A sample has a specific volume of $5.2 \text{ (m}^3\text{)(kg}^{-1}\text{)}$ and a molar volume of $1160 \text{ (m}^3\text{)(kg mol}^{-1}\text{)}$. Determine the molecular weight of the material.
- *2.22** Five thousand barrels of 28°API gas oil are blended with 20,000 bbl of 15°API fuel oil. What is the density of the mixture in lb/gal and lb/ft^3 ? Assume that the volumes are additive. 1 bbl = 42 gal. The density of water at 60°F is 0.999 g/cm^3 .

$$\text{Specific gravity} \frac{60^\circ\text{F}}{60^\circ\text{F}} = \frac{141.5}{^\circ\text{API} + 131.5}$$

- **2.23** In a handbook you find that the conversion between $^\circ\text{API}$ and density is $0.800 \text{ density} = 45.28^\circ\text{API}$. Is this a misprint?
- *2.24** The specific gravity of acetic acid is 1.049. What is the density in lb_m/ft^3 ?
- *2.25** The specific gravity of a fuel oil is 0.82. What is the density of the oil in lb/ft^3 ? Show all units.
- *2.26** The specific gravity of Ag_2O is 7.30 with the reference H_2O at 25°C . What is the specific gravity if the reference water is at 4°C ?
- *2.27** The *Handbook of Physics and Chemistry* lists in one column a 30% sulfuric acid solution at 20°C as having a specific gravity of 1.2185. In the next column it lists the grams/liter of H_2SO_4 in the solution as being equal to 365.6. Is this value correct?
- *2.28** The Federal Water Pollution Control Act, P.L. 92-500, specifies legally acceptable methods for wastewater analysis. Analysis for cyanide is done according to the method outlined in "Standard Methods for the Examination of Water Wastewater." Mercuric chloride is used in the analytic procedure to decompose complex cyanides, and 200 mg are used per analysis.

The Illinois Pollution Control Board has established Water Quality Standards that limit mercury (as Hg) to 0.0005 ppm in any effluent. Permit holders are required to submit daily reports on their effluent. Will a permit holder discharging 100,000 gal/day be in violation of the cited standard if one analysis is made?

- **2.29** You are asked to make up a laboratory solution of 0.10 molar H_2SO_4 (0.10 mol $\text{H}_2\text{SO}_4/\text{L}$) from concentrated (96.0%) H_2SO_4 . You look up the specific gravity of 96.0% H_2SO_4 and find it is 1.858. Calculate
- the weight of 96.0% acid needed per L of solution.
 - the volume of 96.0% acid used per L of solution.
 - the density of the 0.1 molar solution.
- ***2.30** A bartender claims that his special brand of rum is so strong that ice cubes sink in it. Is this possible?
- *2.31** The density of benzene at 60°F is 0.879 g/cm³. What is the specific gravity of benzene at 60°F/60°F?
- **2.32** A liquid has a specific gravity of 0.90 at 25°C. What is its
- Density at 25°C in kg/m³?
 - Specific volume at 25°C in ft³/lb_m?
 - If the liquid is placed in a 1.5-L bottle that has a mass of 232 g, how much will the full bottle weigh?
- **2.33** Given a water solution that contains 1.704 kg of $\text{HNO}_3/\text{kg H}_2\text{O}$ and has a specific gravity of 1.382 at 20°C, express the composition in the following ways:
- Weight percent HNO_3
 - Pounds HNO_3 per cubic foot of solution at 20°C
 - Molarity (gram moles of HNO_3 per liter of solution at 20°C)
- *2.34** OSHA (Occupational Safety and Health Administration) has established limits for the storage of various toxic or hazardous chemicals (OSHA 29 CFR 1910.119, Appendix A). The maximum limit for acetaldehyde is 113.0 kg. What is the minimum size spherical vessel that can be used to store this liquid at room temperature?
- *2.35** For the purpose of permit compliance, all hazardous materials are categorized into three hazard categories: toxicity, flammability, and reactivity, and assigned numbers in each category from 0 to 4 (most severe). Methyl alcohol (methanol, CH_3OH) has the code 1, 4, 0 in the liquid state. For the toxic category, any amount of stored toxic material of category 1 over 0.35 oz. must be reported by city ordinance. Must a one-half liter bottle of methanol (sp.gr. = 0.792) be reported?
- *2.36** Oil (sp.gr. = 0.8) is flowing through a 6 inch diameter pipe with a velocity of 56.7 ft/s. What is the flowrate of the oil in m³/s?
- *2.37** Forty gal/min of a hydrocarbon fuel having a specific gravity of 0.91 flow into a tank truck with load limit of 40,000 lb of fuel. How long will it take to fill the tank in the truck?
- **2.38** Calculate the empirical formula of an organic compound with the following mass analysis: carbon, 26.9%; hydrogen, 2.2%; and oxygen as the only other element present.
- **2.39** Given the following mass percent composition, determine the empirical formula: 49.5% C; 5.2%H; 28.8%N; 16.5%O.

- *2.40 Calculate the mass and mole fractions of the respective components in NaClO_3 .
- *2.41 The specific gravity of a solution of KOH at 15°C is 1.0824 and contains 0.813 lb KOH per gal of solution. What are the mass fractions of KOH and H_2O in the solution?
- **2.42 Prepare an expression that converts mass (weight) fraction (ω) to mole fraction (x), and another expression for the conversion of mole fraction to mass fraction, for a binary mixture.
- *2.43 You have 100 kilograms of gas of the following composition:

CH_4	30%
H_2	10%
N_2	60%

What is the average molecular weight of this gas?

- *2.44 You analyze the gas in 100 kg of gas in a tank at atmospheric pressure, and find the following:

CO_2 : 19.3%, N_2 : 72.1% O_2 : 6.5%, H_2O : 2.1%

What is the average molecular weight of the gas?

- *2.45 Suppose you are required to make an analysis of 317 lb of combustion gas and find it has the following composition:

CO_2	60%
CO	10%
N_2	30%

What is the average molecular weight of this gas in the American Engineering System of units?

- *2.46 You purchase a tank with a volume of 2.1 ft^3 . You pump the tank out, and add first 20 lb. of CO_2 and then 10 lb of N_2 . What is the analysis of the final gas in the tank?
- *2.47 How many ppb are there in 1 ppm? Does the system of units affect your answer? Does it make any difference if the material for which the ppb are measured is a gas, liquid, or solid?
- *2.48 The table lists values of Fe, Cu, and Pb in Christmas wrapping paper for two different brands. Convert the ppm to mass fractions on a paper free basis.

	Concentration, ppm		
	Fe	Cu	Pb
Brand A	1310	2000	2750
Brand B	350	50	5

- *2.49 Harbor sediments in the New Bedford, Massachusetts, area contain PCBs at levels up to 190,000 ppm according to a report prepared by Grant Weaver of the Massachusetts Coastal Zone Management Office (*Environ. Sci. Technol.*, 16(9) (1982):491A. What is the concentration in percent?

- *2.50 NIOSH sets standards for CCl_4 in air at 12.6 mg/m^3 of air (a time weighted average over 40 hr). The CCl_4 found in a sample is 4800 ppb (parts per billion; billion = 10^9). Does the sample exceed the NIOSH standard? Be careful!
- *2.51 The following table shows the annual inputs of phosphorus to Lake Erie:

	Short tons/yr
Source	
Lake Huron	2,240
Land drainage	6,740
Municipal waste	19,090
Industrial waste	<u>2,030</u>
	30,100
Outflow	<u>4,500</u>
Retained	25,600

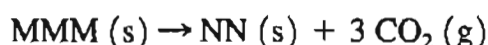
- (a) Convert the retained phosphorus to concentration in micrograms per liter assuming that Lake Erie contains 1.2×10^{14} gal of water and that the average phosphorus retention time is 2.60 yr.
- (b) What percentage of the input comes from municipal water?
- (c) What percentage of the input comes from detergents, assuming they represent 70% of the municipal waste?
- (d) If 10 ppb of phosphorus triggers nuisance algal blooms, as has been reported in some documents, would removing 30% of the phosphorus in the municipal waste and all the phosphorus in the industrial waste be effective in reducing the eutrophication (i.e., the unwanted algal blooms) in Lake Erie?
- (e) Would removing all the phosphate in detergents help?
- *2.52 A gas contains 350 ppm of H_2S in CO_2 . If the gas is liquified, what is the weight fraction H_2S ?
- *2.53 Sulfur trioxide (SO_3) can be absorbed in sulfuric acid solution to form more concentrated sulfuric acid. If the gas to be absorbed contains 55% SO_3 , 41% N_2 , 3% SO_2 , and 1% O_2 , how many parts per million of O_2 are there in the gas? (b) What is the composition of the gas on a N_2 free basis?
- *2.54 If the concentration of Ca is 56.4 mg/L and of Mg is 8.8 mg/L in water, what is the total hardness of the water expressed in mg/L of CaCO_3 ?
- *2.55 Twenty-seven pounds (27 lb) of chlorine gas is used for treating 750,000 gallons of water each day. The chlorine used up by the microorganisms in the water is measured to be 2.6 mg/L. What is the residual (excess) chlorine concentration in the treated water?
- *2.56 A newspaper report says the FDA found 13-20 ppb of acrylonitrile in a soft drink bottle, and if this is correct, it only amounts to 1 molecule of acrylonitrile per bottle. Is this statement correct?
- *2.57 Several studies of global warming indicate that the concentration of CO_2 in the atmosphere is increasing by roughly 1% per year. Do we have to worry about the decrease in the oxygen concentration also?

- *2.58 The analysis of a biomass sample gave

	% dry weight of cell
C	50.2
O	20.1
N	14.0
H	8.2
P	3.0
Other	4.5

This compound gives a ratio of 10.5 g cells/mol ATP synthesized in the metabolic reaction to form cells. Approximately how many moles of C are in the cells per mole of ATP?

- *2.59 A radioactive tracer labeled microorganism (MMM) decomposes to NN as follows



If the $\text{CO}_2 \text{ (g)}$ yields 2×10^7 dpm (disintegrations per minute) in a detection device, how many μCi (micro Curies) is this? How many cpm (counts per minute) will be noted if the counting device is 80% efficient in counting disintegrations? Data: 1 Curie = 3×10^{10} dps (disintegrations per second).

- *2.60 Several alternative compounds have been added to gasoline including methanol, ethanol, and methy-ter-butyl ether (MTBE) to increase the oxygen content of gasoline in order to reduce the formation of CO on combustion. Unfortunately, MTBE has been found in ground water at concentrations sufficient to cause concern. Persistence of a compound in water can be evaluated from its half-life, $t_{1/2}$, i.e., the time for one-half of the compound to leave the system of interest. The half-life depends on the conditions in the system, of course, but for environmental evaluation can be approximated by

$$t_{1/2} = \ln(2)/(k)(\text{OH}^-)$$

where (OH^-) is the concentration of hydroxyl radical in the system that for this problem of the contamination of water is equal to 1.5×10^6 molecules/ cm^3 . The values of k determined from experiment are:

	$k \text{ (cm}^3\text{)/(molecule)(sec)}$
Methanol	0.15×10^{-12}
Ethanol	1×10^{-12}
MTBE	0.60×10^{-12}

Calculate the half-life of each of the three compounds, and order them according to their persistence.

CHAPTER 3

CHOOSING A BASIS

Your objectives in studying this chapter are to be able to:

1. State the three questions useful in selecting a basis.
2. Apply the three questions to problems to select a suitable basis or sequence of bases.

Have you noted in some of the examples in Chapter 2 that the word **basis** has appeared at the start of the examples? The concept of a basis is vitally important to both your understanding of how to solve a problem and to your solving it in the most expeditious manner.

Looking Ahead

In this section we discuss how you choose a basis on which to solve problems.

Main Concepts

A basis is a reference chosen by you for the calculations you plan to make in any particular problem, and a proper choice of basis frequently makes the problem much easier to solve. The basis may be a period of time such as hours, or a given mass of material, such as 5 kg of CO_2 , or some other convenient quantity. To select a sound basis (which in many problems is predetermined for you but in some problems is not so clear), ask yourself the following three questions:

- a. What do I have to start with? (e.g., I have 100 lb of oil; I have 46 kg of fertilizer).
- b. What answer is called for? (e.g., How much product is produced per hour?).
- c. What is the most convenient basis to use? (For example, suppose that the mole fractions of an amount of material are known. Then selecting 100 kilogram moles of the material as a basis would make sense. On the other hand, if the

mass fractions of the material are known, then 100 kg of the material would be an appropriate basis).

If a rate of flow or production of a material is stated in a problem, then you should usually select the time interval, such as 1 minute or 1 hour, as the basis on which to make the calculations, because then a time unit does not have to be dragged along during all of the calculations.

These questions and their answers will suggest suitable bases. Sometimes when several bases seem appropriate, you may find it is best to use a unit basis of 1 or 100 of something, as, for example, kilograms, hours, moles, or cubic feet. For liquids and solids in which a mass (weight) analysis applies, a convenient basis is often 1 or 100 lb or kg; similarly, 1 or 100 moles is often a good choice for a gas. The reason for these choices is that the fraction or percent in the analysis of the material automatically equals the number of pounds, kilograms, or moles, respectively, and one step in the calculations is saved.

Always state the basis you have chosen for your calculations by writing it prominently on your calculation sheets (or computer screen).

EXAMPLE 3.1 Choosing a Basis

The dehydration of the lower alkanes can be carried out using a ceric oxide (CeO) catalyst. What is the mass fraction and mole fraction of Ce and O in the catalyst?

Solution

Start the solution by selecting a basis. Because no specific amount of material is specified, the question what do I have to start with does not help decide on a basis. Neither does the question about the desired answer. Thus, selecting a convenient basis becomes the best choice for a basis. What do you know about CeO ? You know from the formula that one mole of Ce is combined with one mole of O. Consequently, a basis of 2 kg mol (or 2 g mol, or 2 lb mol, etc.) would make sense. You can get the atomic weights for Ce and O from Appendix B, and then you are prepared to calculate the respective masses of Ce and O in CeO . The calculations are presented in the form of the following table:

Basis: 2 kg mol of CeO

Component	kg mol	Mole fraction	Mol. wt.	kg.	Mass fraction
Ce	1	0.50	140.12	140.12	0.90
O	1	0.50	16.0	16.0	0.10
Total	2	1.00	156.1	156.1	1.00

EXAMPLE 3.2 Choosing a Basis

Most processes for producing high-energy-content gas or gasoline from coal include some type of gasification step to make hydrogen or synthesis gas. Pressure gasification is preferred because of its greater yield of methane and higher rate of gasification.

Given that a 50.0 kg test run of gas averages 10.0% H₂, 40.0% CH₄, 30.0% CO, and 20.0% CO₂, what is the average molecular weight of the gas?

Solution

Let's choose a basis. The answer to question 1 is to select a basis of 50.0 kg of gas ("what I have to start with"), but is this choice a good basis? A little reflection will show that such a basis is of no use. You cannot multiply the given *mole percent* of this gas (remember that the composition of gases is given in mole percent unless otherwise stated) times kg and expect the result to mean anything. Try it, being sure to include the respective units. Thus, the next step is to choose a "convenient basis," which is 100 kg mol of gas, and proceed as follows:

Basis: 100 kg mol or lb mol of gas

Set up a table such as the following to make a compact presentation of the calculations. You do not have to—you can make individual computations for each component, but such a procedure is inefficient and more prone to errors.

Component	Percent = kg mol or lb mol	Mol wt.	Kg or lb
CO ₂	20.0	44.0	880
CO	30.0	28.0	840
CH ₄	40.0	16.04	642
H ₂	10.0	2.02	20
Total	100.0		2382

$$\text{Average molecular weight} = \frac{2382 \text{ kg}}{100 \text{ kg mol}} = 23.8 \text{ kg/kg mol}$$

Check the solution by noting that an average molecular weight of 23.8 is reasonable since the molecular weights of the components varies from 10 to 40.

EXAMPLE 3.3 Choosing a Basis for Cell Growth

In measuring the growth rate of cells in the laboratory, you inject 50,000 cells into a well in a so called well plate. Next you add tritiated thymidine to the culture in the well, and 24 hours later the radiation from the cells in the well reads 5000 cpm (counts per minute) from the uptake of the thymidine by the cells. At the same time total cell count is 60,000 cells.

The final step in the experiment is to add a growth factor to the medium under the same initial conditions (50,000 cells in a well). After 24 hours the radiation count per well is 8000 cpm. You are asked to compute the increase in average growth rate by adding the growth factor. What would be a good basis on which to solve the problem?

Solution

This problem involves amounts (numbers of cells in the well and counts of the disintegrations of radioactive material) and times (minutes and hours). A convenient basis to select would be a time, say 1 or 24 hours, because several given quantities of cells are specified. Choose 1 hour.

As a matter of interest, without the growth factor the average growth rate is the 10,000 cell increase divided by 24 hours, or 417 cells/hr for the selected basis. With the growth factor added, you have to find the final cell count after 24 hours. The assumption in practice is that the cell growth is directly proportional to the tritiated thymidine uptake because thymidine is taken up at each cell division. Thus, based on the nongrowth data,

$$417 \text{ cells} = k (5000 \text{ cpm})$$

and $k = 0.0833 \text{ cells/cpm}$. When the cpm is 8000, the number of cells is

$$(0.0833)(8000) = 667 \text{ cells (in one hour), an increase of 60\%}$$

EXAMPLE 3.4 Calculation of the Mass Fraction of Components in Nanoparticles

The microstructure of nanosized particles has proved to be important in nanotechnology in developing economic magnetic performance of nanocomposites. In a ternary alloy such as $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$ the average grain size is about 30 nm. By replacing 0.2 atoms of Fe with atoms of Cu, the grain size can be reduced (improved) to 17 nm.

- What is the molecular formula of the alloy after adding the Cu to replace the Fe?
- What is the mass fraction of each atomic species in the improved alloy?

Solution

Pick a convenient basis. Because the atoms in the chemical formula of the alloy total to 100, pick a basis of

Basis: 100 g mol (or atoms) of $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$

- The final alloy is $\text{Nd}_{4.5}\text{Fe}_{76.8}\text{B}_{18.5}\text{Cu}_{0.2}$.
- Use a table to calculate the respective mass fractions.

Component	Original g mol	Final g mol	MW	g	Mass fraction
Nd	4.5	4.5	144.24	649.08	0.126
Fe	77	76.8	55.85	4289.28	0.833
B	18.5	18.5	10.81	199.99	0.039
Cu		0.2	63.55	12.71	0.002
Total	100.0	100.0		5151.06	1.000

In summary, be sure to state the basis of your calculations so that you will keep clearly in mind the real nature of your calculations, and so that anyone checking your problem solution will be able to understand on what basis your calculations were performed.

You no doubt have heard the story of Ali Baba and the 40 thieves. Have you heard about Ali Baba and the 39 camels? Ali Baba gave his four sons 39 camels to be divided among them so that the oldest son got one-half the camels; the second son a quarter, the third an eighth, and the youngest a tenth. The four brothers were at a loss as to how they should divide the inheritance until a stranger came riding along on his camel. He added his own camel to Ali Baba's 39 and then divided the 40 among the sons. The oldest son received 20; the second, 10; the third, 5; and the youngest, 4. One camel was left. The stranger mounted it—for it was his own—and rode off. Amazed,

the four brothers watched him ride away. The oldest brother was the first to start calculating. Had his father not willed half of the camels to him? Twenty camels are obviously more than half of 39. One of the four sons must have received less than his due. But figure as they would, each found that he had more than his share.

After agonizing over this problem you will realize that the sum of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{1}{10}$ is not 1 but is 0.975. By adjusting (normalizing) the camel fractions (!) so that they total 1, the division of camels is validated:

Camel fractions	Normalizing		Normalized true fractions			Distributed camels (integer)
0.500	$\left(\frac{0.500}{0.975}\right)$	=	0.5128	×	39	= 20
0.250	$\left(\frac{0.250}{0.975}\right)$	=	0.2564	×	39	= 10
0.125	$\left(\frac{0.125}{0.975}\right)$	=	0.1282	×	39	= 5
0.100	$\left(\frac{0.100}{0.975}\right)$	=	0.1026	×	39	= 4
0.975	$\left(\frac{0.975}{0.975}\right)$	=	1.000			39

What we have done is to change the calculations from a basis of 0.975 to a new basis of 1.000.

More frequently than you probably would like, you will have to change from your original selection of a basis in solving a problem to one or more different bases in order to put together the information needed to solve the problem. For example, given a 1.00 mol of gas containing O_2 (20%), N_2 (78%), and SO_2 (2%), find the composition of the gas on an *SO_2 -free basis*, meaning gas without the SO_2 in it. What you do is to calculate the moles of each component, remove the SO_2 and adjust the basis for the calculations so that the gas becomes composed only of O_2 and N_2 with a percent composition totaling 100%:

Basis: 1.00 mol gas

Components	Mol fraction	Mol	Mol SO_2 free	Mol fraction SO_2 free
O_2	0.20	0.20	0.20	0.20
N_2	0.78	0.78	0.78	0.80
SO_2	0.02	0.02		
	1.00	1.00	0.98	1.00

The round-off in the last column is appropriate given the original values for the mole fractions.

Here is a more complicated example.

EXAMPLE 3.5 Changing Bases

A medium-grade bituminous coal analyzes as follows:

Component	Percent
S	2
N	1
O	6
Ash	11
Water	3
Residuum	77

The residuum is C and H, and the mole ratio in the residuum is $H/C = 9$. Calculate the weight (mass) fraction composition of the coal with the ash and the moisture omitted (ash- and moisture-free).

Solution

To calculate the mass fractions of the components of the coal on an ash and moisture free basis, i.e., omitting the ash and water in coal in the list of compounds, you first have to determine the respective amounts of C and H in the residuum. Then you remove the ash and water from the list of compounds, add up the remaining masses, and calculate the mass fractions of each of the components remaining.

Take as a basis 100 kg of coal because then percent = kilograms.

Basis: 100 kg of coal

The sum of the S + N + O + ash + water is

$$2 + 1 + 6 + 11 + 3 = 23 \text{ kg}$$

You need to determine the individual kg of C and of H in the 77 kg total residuum.

To determine the kilograms of C and H, you have to select a new basis. Is 77 kg or 100 kg satisfactory? No. Why? Because the H/C ratio is given in terms of moles, not weight (mass). Pick instead a convenient basis involving moles.

Basis: 100 kg mol

Component	Mole fraction	kg mol	Mol. wt.	kg	Mass fraction
H	$\frac{9}{1+9} = 0.90$	90	1.008	90.7	0.43
C	$\frac{1}{1+9} = \frac{0.10}{1.00}$	$\frac{10}{100}$	12	$\frac{120}{210.7}$	$\frac{0.57}{1.00}$

On the basis of 100 kg of C+H, we have the kg of H and C, but we need to change the values to mesh with the basis of 100 kg of coal.

Basis: 100 kg of coal

The next step is to calculate the kg of C and H in the 77 kg of the residuum. You can use the mass fractions from the table above, or just use the kg values directly:

$$\text{H: } (77 \text{ kg})(0.43) = 33.15 \text{ kg}$$

$$\text{C: } (77 \text{ kg})(0.57) = 43.85 \text{ kg}$$

Finally, you can prepare a table summarizing the results on the basis of 1.00 kg of the coal ash-free and water-free.

Component	kg	Wt. fraction
C	43.85	0.51
H	33.15	0.39
S	2	0.02
N	1	0.01
O	<u>6</u>	<u>0.07</u>
Total	86.0	1.00

SELF-ASSESSMENT TEST

Questions

1. What are the three questions you should ask yourself in selecting a basis?
2. Why do you sometimes have to change bases during the solution of a problem?

Problems

1. What would be good initial bases to select in solving Examples 1.2, 1.4, 2.1, and 2.2.

Thought Problem

Water-based dust-suppression systems are an effective and viable means of controlling dust and virtually eliminate the historic risk of fires and explosions in grain elevators. Water-based safety systems have resulted in cleaner elevators, improved respiratory atmospheres for employees, and reduced dust emissions into the environment surrounding storage facilities. However, some customers have complained that adding water to the grain causes the buyer to pay too much for the grain. The grain elevator operators argue that all grain shipments unavoidably contain a weight component in the form of moisture. Moisture is introduced to grain and to grain products in a broad variety of practices.

What would you recommend to elevator operators and grain dealers to alleviate this problem?

Looking Back

We posed three questions for you to ask yourself as guides in selecting a good basis to use in solving problems, and gave some examples. We also showed how to change bases if needed during the course of solving a problem.

GLOSSARY OF NEW WORDS

Basis The reference material or time selected to use in making the calculations in a problem.

Changing bases Shifting the basis in a problem from one value to another for convenience in the calculations.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the "Read Me" pages in the front of this book, the following discuss the choice of a basis:

Fogler, H. S. *Elements of Reaction Engineering*, Prentice-Hall, Upper Saddle River, N.J. (1999).

Henley, E. J., and H. Bieber. *Chemical Engineering Calculations*, McGraw-Hill, New York (1959).

PROBLEMS

***3.1** Read each of the following problems, and select a suitable basis for solving each one. Do not solve the problems.

- (a) You have 130 kg of gas of the following composition: 40% N_2 , 30% CO_2 , and 30% CH_4 in a tank. What is the average molecular weight of the gas?
- (b) You have 25 lb of a gas of the following composition:

CH_4	80%
C_2H_4	10%
C_2H_6	10%

What is the average molecular weight of the mixture? What is the weight (mass) fraction of each of the components in the mixture?

- (c) The proximate and ultimate analysis of a coal is given in the table. What is the composition of the "Volatile Combustible Matter (VCM)"? Present your answer in the form of the mass percent of each element in the VCM.

Proximate Analysis (%)		Ultimate Analysis (%)	
Moisture	3.2	Carbon	79.90
Volatile Combustible matter (VCM)	21.0	Hydrogen	4.85
Fixed Carbon	69.3	Sulfur	0.69
Ash	6.5	Nitrogen	1.30
		Ash	6.50
		Oxygen	6.76
Total	100.0	Total	100.00

- (d) A fuel gas is reported to analyze, on a mole basis, 20% methane, 5% ethane, and the remainder CO_2 . Calculate the analysis of the fuel gas on a mass percentage basis.
- 65 ✓ (e) A gas mixture consists of three components: argon, B, and C. The following analysis of this mixture is given:

40.0 mol % argon
 18.75 mass % B
 20.0 mol % C

The molecular weight of argon is 40 and the molecular weight of C is 50. Find:

- (a) The molecular weight of B
 (b) The average molecular weight of the mixture.

- 66 ✓ ****3.2** Two engineers are calculating the average molecular weight of a gas mixture containing oxygen and other gases. One of them uses the correct molecular weight of 32 for oxygen and determines the average molecular weight as 39.2. The other uses an in-

correct value of 16 and determines the average molecular weight as 32.8. This is the only error in his calculations. What is the percentage of oxygen in the mixture expressed as mol %? Choose a basis to solve the problem; do not solve it.

- *3.3** Choose a basis for the following problem. Chlorine usage at a water treatment plant averages 134.2 lb/day. The average flow rate of the water leaving the plant is 10.7 million gallons per day. What is the average chlorine concentration in the treated water leaving the plant expressed in mg/L?

CHAPTER 4

TEMPERATURE

Your objectives in studying this chapter are to be able to:

1. Define what temperature is.
2. Explain the difference between absolute and relative temperature.
3. Convert a temperature in any of the four common scales ($^{\circ}\text{C}$, K, $^{\circ}\text{F}$, $^{\circ}\text{R}$) to any of the others.
4. Convert an expression involving units of temperature and temperature difference to other units of temperature and temperature difference.
5. Know the reference points for the four temperature scales.

You know what temperature is from past physics and chemistry courses, hence you might well ask: why are we discussing it again? Unfortunately, certain characteristics of temperature exist that in our experience cause confusion for introductory engineering students. We want to elucidate these issues.

Looking Ahead

In this chapter we first discuss temperature scales and then take up the issue of converting from one temperature scale to another.

Main Concepts

You can hardly go through a single day without noticing or hearing what the temperature is. Believe it or not, considerable controversy exists among some scientists as to what the correct definition of **temperature** is (consult some of the references at the end of this chapter for further information). Some scientists prefer to say that temperature is a measure of the energy (mostly kinetic) of the molecules in a system. This definition tells us about the amount of energy. Other scientists prefer to say that temperature is a property of the state of thermal equilibrium of the system with respect to other systems because temperature tells us about the capability of a

system to transfer energy (as heat). When you get to Chapter 21 you will find out, if you do not already know, that a big difference exists between these two concepts.

In this book we use four types of temperature, two based on a relative scale, degrees **Fahrenheit** ($^{\circ}\text{F}$) and **Celsius** ($^{\circ}\text{C}$), and two based on an absolute scale, degree **Rankine** ($^{\circ}\text{R}$) and **kelvin** (K). Note that the degree symbol ($^{\circ}$) is not used with the kelvin temperature abbreviation K. Relative scales are the ones you hear the TV or radio announcer give, and are based on a specified reference temperature (32°F or 0°C) that occurs in an ice-water mixture (the freezing point of water).

Absolute temperature scales have their zero point at the lowest possible temperature that we believe can exist. As you may know, this lowest temperature is related both to the ideal gas laws and to the laws of thermodynamics. The absolute scale, based on degree units the size of those in the Celsius scale, is called the kelvin scale in honor of Lord Kelvin (1824–1907) who reconciled the divergent views of the principle of the conservation of energy. The absolute scale, which corresponds to the Fahrenheit degree units, is called the *Rankine* scale in honor of W. J. M. Rankine (1820–1872), a Scottish engineer. Figure 4.1 illustrates the relationship between relative temperature and absolute temperature. We shall usually round off absolute zero on the Rankine scale of -459.67°F to -460°F ; similarly, -273.15°C frequently will be rounded off to -273°C . In Figure 4.1 all of the values of the temperatures have been rounded off, but more significant figures can be used. 0°C and its equivalents are known as the values of the **standard conditions of temperature**.

Now we turn to a topic that causes endless difficulty in temperature conversion because of confusing semantics and notation. To start, you should recognize that the unit degree (i.e., the unit temperature difference or division) on the Kelvin-Celsius scale is not the same size as that on the Rankine-Fahrenheit scale. If we let $\Delta^{\circ}\text{F}$ represent the unit temperature difference in the Fahrenheit scale and $\Delta^{\circ}\text{R}$ be the unit temperature difference in the Rankine scale, and $\Delta^{\circ}\text{C}$ and ΔK be the analogous units in the other two scales, you probably are aware that

$$\Delta^{\circ}\text{F} = \Delta^{\circ}\text{R}$$

$$\Delta^{\circ}\text{C} = \Delta\text{K}$$

Also, if you keep in mind that the $\Delta^{\circ}\text{C}$ is larger than the $\Delta^{\circ}\text{F}$

$$\frac{\Delta^{\circ}\text{C}}{\Delta^{\circ}\text{F}} = 1.8 \quad \text{or} \quad \Delta^{\circ}\text{C} = 1.8 \Delta^{\circ}\text{F}$$

$$\frac{\Delta\text{K}}{\Delta^{\circ}\text{R}} = 1.8 \quad \text{or} \quad \Delta\text{K} = 1.8 \Delta^{\circ}\text{R}$$

Thus, when we cite the temperature of a substance we are **stating the cumulative number of units of the temperature scale that occur** (an enumeration of ΔT s) **measured from the reference point**. Reexamine Figure 4.1.

$$T_{\circ\text{F}} = a_{\circ\text{F}} + \left(\frac{1.8 \Delta^{\circ}\text{F}}{\underbrace{\Delta^{\circ}\text{C}}_b} \right) T_{\circ\text{C}}$$

Unfortunately, the units for b are usually ignored; just the value of b (1.8) is employed.

When you reach Chapter 21 you will note that the heat capacity in the SI system has the units of $\text{J}/(\text{g mol})(\text{K})$. Does the K in the heat capacity designate the temperature in degrees K or the unit interval ΔK ? In this case K represents a temperature difference. Consider the gas constant, R , which can have units of $(\text{kg})(\text{m}^2)/(\text{kg mol})(\text{s}^2)(\text{K})$. Does K represent the temperature in degrees K or the interval ΔK ? You should recall for the ideal gas that you use the absolute temperature.

If you are not well acquainted with temperature conversion, be sure to practice conversions until they become routine. Many calculators and computers make the conversions automatically, but you should know that

$$T_{\circ\text{R}} = T_{\circ\text{F}} \left(\frac{1 \Delta^{\circ}\text{R}}{1 \Delta^{\circ}\text{F}} \right) + 460^{\circ}\text{R} \quad (1.6)$$

$$T_{\text{K}} = T_{\circ\text{C}} \left(\frac{1 \Delta\text{K}}{1 \Delta^{\circ}\text{C}} \right) + 273 \text{ K} \quad (1.7)$$

$$T_{\circ\text{F}} - 32^{\circ}\text{F} = T_{\circ\text{C}} \left(\frac{1.8 \Delta^{\circ}\text{F}}{1 \Delta^{\circ}\text{C}} \right) \quad (1.8)$$

$$T_{\circ\text{C}} = (T_{\circ\text{F}} - 32^{\circ}\text{F}) \left(\frac{1 \Delta^{\circ}\text{C}}{1.8 \Delta^{\circ}\text{F}} \right) \quad (1.9)$$

Now let us look at some examples.

EXAMPLE 4.1 Temperature Conversion

Convert 100°C to (a) K, (b) $^{\circ}\text{F}$, and (c) $^{\circ}\text{R}$.

Solution

$$(a) (100 + 273)^{\circ}\text{C} \frac{1 \Delta\text{K}}{1 \Delta^{\circ}\text{C}} = 373 \text{ K}$$

or with suppression of the Δ symbol,

$$(100 + 273)^{\circ}\text{C} \frac{1 \text{ K}}{1^{\circ}\text{C}} = 373 \text{ K}$$

$$(b) (100^{\circ}\text{C}) \frac{1.8 \Delta^{\circ}\text{F}}{1 \Delta^{\circ}\text{C}} + 32^{\circ}\text{F} = 212^{\circ}\text{F}$$

$$(c) (212 + 460)^{\circ}\text{F} \frac{1 \Delta^{\circ}\text{R}}{1 \Delta^{\circ}\text{F}} = 672^{\circ}\text{R}$$

or

$$(373 \text{ K}) \frac{1.8 \Delta^{\circ}\text{R}}{1 \Delta\text{K}} = 672^{\circ}\text{R}$$

EXAMPLE 4.2 Temperature Conversion

The heat capacity of sulfuric acid has the units $\text{J}/(\text{g mol})(^{\circ}\text{C})$, and is given by the relation

$$\text{heat capacity} = 139.1 + 1.56 \times 10^{-1}T$$

where T is expressed in $^{\circ}\text{C}$. Modify the formula so that the resulting expression has the associated units of $\text{Btu}/(\text{lb mol})(^{\circ}\text{R})$ and T is in $^{\circ}\text{R}$.

Solution

The symbol $^{\circ}\text{C}$ in the denominator of the heat capacity stands for the unit temperature difference, $\Delta^{\circ}\text{C}$, not the temperature, whereas the units of T in the equation are in $^{\circ}\text{C}$. First you have to substitute the proper equation in the formula to convert T in $^{\circ}\text{C}$ to T in $^{\circ}\text{R}$, and then by multiplication by conversion factors convert the units on the righthand side of the equation to $\text{Btu}/(\text{lb mol})(^{\circ}\text{R})$ as requested.

$$\begin{aligned} \text{heat capacity} &= \left\{ 139.1 + 1.56 \times 10^{-1} \overbrace{\left[(T_{^{\circ}\text{R}} - 460 - 32) \frac{1}{1.8} \right]}^{T_{^{\circ}\text{C}}} \right\} \\ &\times \underbrace{\frac{1 \text{ J}}{(\text{g mol})(^{\circ}\text{C})} \left| \frac{1 \text{ Btu}}{1055 \text{ J}} \right| \frac{454 \text{ g mol}}{1 \text{ lb mol}} \left| \frac{1^{\circ}\text{C}}{1.8^{\circ}\text{R}} \right|}_{\text{conversion factors}} = 23.06 + 2.07 \times 10^{-2}T_{^{\circ}\text{R}} \end{aligned}$$

Note the suppression of the Δ symbol in the conversion between $\Delta^{\circ}\text{C}$ and $\Delta^{\circ}\text{R}$.

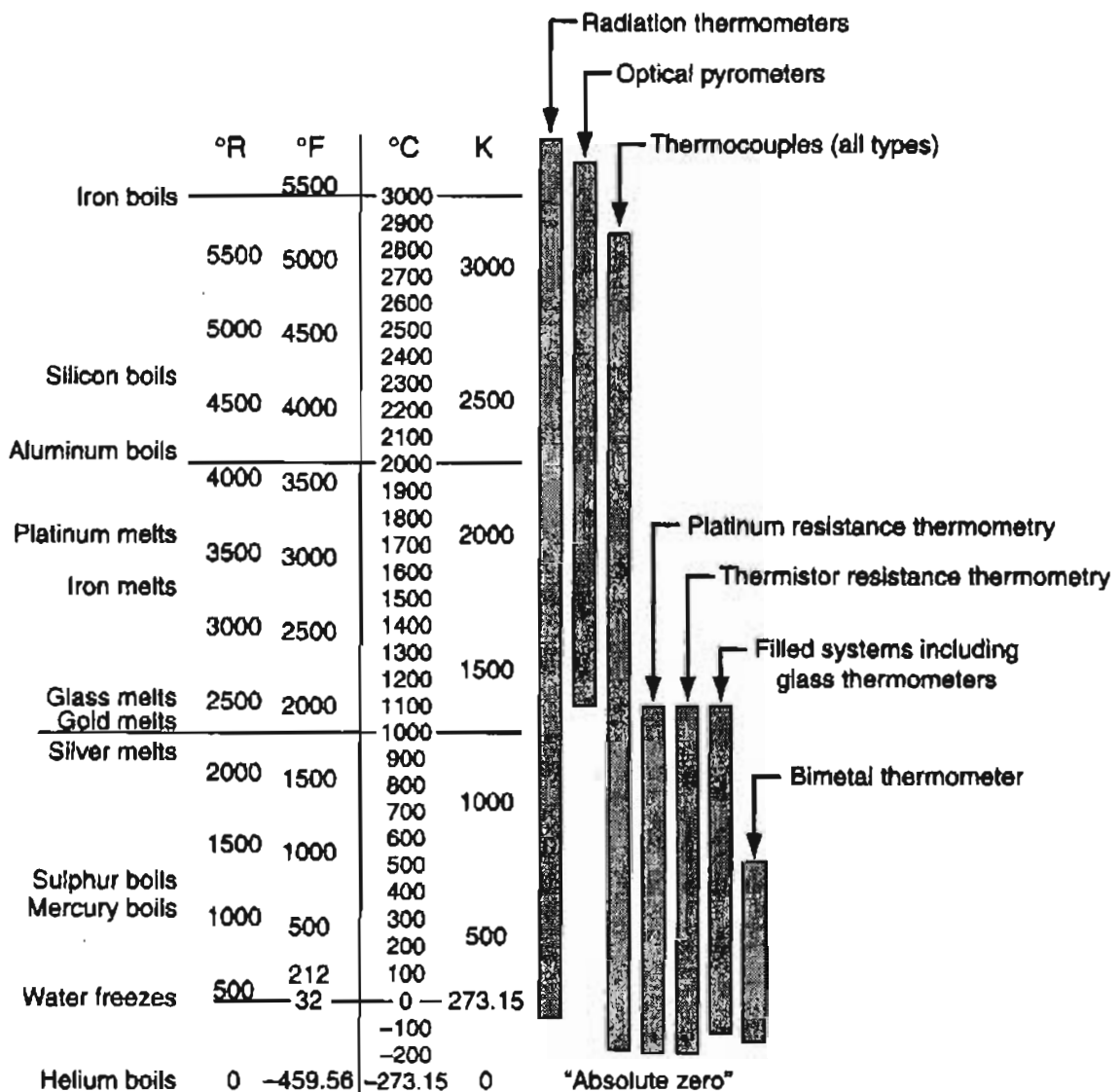


Figure 4.2. Temperature measuring instruments span the range from near absolute zero to beyond 3000 K. The chart indicates the preferred methods of thermal instrumentation for various temperature regions.

Whatever temperature scale you employ, to be useful in engineering, the temperature has to be measured. Look at Figure 4.2 to see the useful range of several measuring techniques.

SELF-ASSESSMENT TESTS

Questions

1. What are the reference points of (a) the Celsius and (b) the Fahrenheit scales?
2. How do you convert a *temperature difference*, Δ , from Fahrenheit to Celsius?

3. Is the unit temperature difference $\Delta^{\circ}\text{C}$ a larger interval than $\Delta^{\circ}\text{F}$? Is 10°C higher than 10°F ?
4. In Appendix E, the heat capacity of sulfur is $C_p = 15.2 + 2.68T$, where C_p is in $\text{J}/(\text{g mol})(\text{K})$ and T is in K. Convert this expression so that C_p is in $\text{cal}/(\text{g mol})(^{\circ}\text{F})$ with T in $^{\circ}\text{F}$.
5. Suppose that you are given a tube partly filled with an unknown liquid and are asked to calibrate a scale on the tube in $^{\circ}\text{C}$. How would you proceed?
6. Answer the following questions:
 - (a) In relation to absolute zero, which is higher, 1°C or 1°F ?
 - (b) In relation to 0°C , which is higher, 1°C or 1°F ?
 - (c) Which is larger, $1\Delta^{\circ}\text{C}$ or $1\Delta^{\circ}\text{F}$?

Problems

1. Complete the following table with the proper equivalent temperatures:

$^{\circ}\text{C}$	$^{\circ}\text{F}$	K	$^{\circ}\text{R}$
-40	_____	_____	_____
_____	77.0	_____	_____
_____	_____	698	_____
_____	_____	_____	69.8

Thought Problems

1. In reading a report on the space shuttle you find the statement that "the maximum temperature on reentry is 1482.2°C ." How many significant figures do you think are represented by this temperature?
2. What temperature-measuring devices would you recommend to make the following measurements:
 - (a) temperature of the thermal decomposition of oil shale (300° to 500°C)
 - (b) air temperature outside your home (-20° to 30°C)
 - (c) temperature inside a freeze-drying apparatus (-100° to 0°C)
 - (d) flame temperature of a Bunsen burner (2000° to 2500°C)
3. A vacuum tower used to process residual oil experienced severe coking (carbon formation) on the tower internals when it rained. Coking occurs because the temperature of the fluid gets to be too high. The temperature of the entering residual was controlled by a temperature recorder-controller (TRC) connected to a thermocouple inserted onto a Thermowell in the pipeline bringing the residual into the column. The TRC was operating at 700°F , whereas the interior of the column was at 740°F (too hot). What might be the problem?

Discussion Problems

1. In the book by Eric Rogers (*Physics for the Inquiring Mind*, Princeton University Press, Princeton, NJ, 1960), temperature is defined as: "the hotness measured in some definite scale." Is this correct? How would you define temperature?
2. In the kelvin or Rankine (absolute temperature) scales, the relation used for temperature is $T = n\Delta T$, where ΔT is the value of the unit temperature and n is the number of units enumerated. When $n = 0$, $T = 0$. Suppose that temperature is defined by the relation for $\ln(T) = n\Delta T$. Does $T = 0$ occur? What does $n = 0$ mean? Does the equivalent of absolute zero kelvin exist?

Looking Back

In this chapter we explained the difference between the absolute and relative temperature scales. We pointed out how you must be careful in distinguishing between the unit temperature difference and the temperature itself, especially when converting units.

GLOSSARY OF NEW WORDS

Celsius ($^{\circ}\text{C}$) Relative temperature scale with zero degrees being the freezing point of an air-water mixture.

Fahrenheit ($^{\circ}\text{F}$) Relative temperature scale with 32 degrees being the freezing point of an air-water mixture.

Kelvin (K) Absolute temperature scale based on zero degrees being the lowest possible temperature we believe can exist.

Rankine ($^{\circ}\text{R}$) Absolute temperature scale related to degrees Fahrenheit based on zero degrees being the lowest possible temperature we believe can exist.

Standard conditions of temperature 0°C , 32°F , 273.15 K , and 459.67°R .

Temperature A measure of the energy of the molecules in a system.

Temperature interval (ΔT) Size of one degree in a temperature scale.

SUPPLEMENTARY REFERENCES

Gilabert, M. A., and J. Pellicer. "Celsius or Kelvin: Something to Get Steamed Up About," *Phys. Educ.* **31**, 52–55 (1996).

Michalski, L. (ed.). *Temperature Measurement*, John Wiley, New York (2001).

- Pellicer, J., M. Ampano Gilabert, and E. Lopez-Baeza. "The Evolution of the Celsius and Kelvin Scales and the State of the Art," *J. Chem. Educ.*, **76**, 911–913 (1999).
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- Romer, R. H. "Temperature Scales," *The Physics Teacher*, 450 (October 1982).
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Web Pages

<http://www.santesson.com/engtemp.html>
<http://www.sciencemadesimple.net/temperature.html>
<http://www.inidata.ucar.edu/staff/blynds/tmp.html>
<http://www.temperatures.com>

PROBLEMS

- *4.1 "Japan, U.S. Aim for Better Methanol-Powered Cars," read the headline in the *Wall Street Journal*. Japan and the U.S. plan to join in developing technology to improve cars that run on methanol, a fuel that causes less air pollution than gasoline. An unspecified number of researchers from Japanese companies will work with the EPA to develop a methanol car that will start in temperatures as low as minus 10 degrees Celsius. What is this temperature in degrees Rankine, kelvin, and Fahrenheit?
- **4.2 Can negative temperature measurements exist?
- **4.3 The heat capacity C_p of acetic acid in J/(g mol)(K) can be calculated from the equation

$$C_p = 8.41 + 2.4346 \times 10^{-5}T$$

where T is in K. Convert the equation so that T can be introduced into the equation in °R instead of K. Keep the units of C_p the same.

- *4.4 Convert the following temperatures to the requested units:
- 10°C to °F
 - 10°C to °R
 - 25°F to K
 - 150K to °R
- *4.5 Heat capacities are usually given in terms of polynomial functions of temperature. The equation for carbon dioxide is

$$C_p = 8.4448 + 0.5757 \times 10^{-2}T - 0.2159 \times 10^{-5}T^2 + 0.3059 \times 10^{-9}T^3$$

where T is in °F and C_p is in Btu/(lb mol)(°F). Convert the equation so that T can be in °C and C_p will be in J/(g mol)(K).

- *4.6 In a report on the record low temperatures in Antarctica, *Chemical and Engineering News* said at one point that "the mercury dropped to –76°C." In what sense is that possible? Mercury freezes at –39°C.

****4.7** "Further, the degree Celsius is exactly the same as a kelvin. The only difference is that zero degree Celsius is 273.15 kelvin. Use of Celsius temperature gives us one less digit in most cases" from [*Eng. Educ.*, (April 1977):678]. Comment on the quotation. Is it correct? If not, in what way or sense is it wrong?

***4.8** Calculate all temperatures from the one value given:

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
°F	140				1000			
°R			500			1000		
K		298					1000	
°C				-40				1000

****4.9** The emissive power of a blackbody depends on the fourth power of the temperature and is given by

$$W = AT^4$$

where W = emission power, Btu/(ft²)(hr)

A = Stefan-Boltzman constant, 0.171×10^{-8} Btu/(ft²)(hr)(°R)⁴

T = temperature, °R

What is the value of A in the units J/(m²)(s)(K⁴)?

***4.10** Suppose that an alcohol and a mercury thermometer read exactly 0°C at the ice point and 100°C at the boiling point. The distance between the two points is divided into 100 equal parts in both thermometers. Do you think these thermometers will give exactly the same reading at a temperature of, say, 60°C? Explain.

****4.11** For the following data plot p vs. $1/T$. Do you get a straight line? Try $\ln(p)$ vs. $1/T$ and repeat. Use curve fitting software (refer to the CD accompanying this book) to estimate the values of the coefficients in the relation

$$\ln(p) = a + b(1/T)$$

T is in K and p is in mm Hg absolute.

T (K)	p (mm Hg)
273	5
298	24
323	93
373	760

Predict the value of p at 1340 mm Hg.

CHAPTER 5

PRESSURE

5.1 Pressure and Its Units	100
5.2 Measurement of Pressure	103
5.3 Differential Pressure Measurements	114

Your objectives in studying this chapter are to be able to:

1. Define pressure, atmospheric pressure, barometric pressure, standard pressure, and vacuum.
2. Explain the difference between absolute and relative (gauge pressure).
3. List four ways to measure pressure.
4. Convert from gauge to absolute pressure and vice versa.
5. Convert a pressure measured in one set of units to another set, including kPa, mm Hg, ft H₂O, atm, in. Hg, and psi using the standard atmosphere or density ratios of liquids.
6. Calculate the pressure from the density and height of a column of static fluid.

Why review pressure, a topic you no doubt have encountered many times before? Our experience has shown that a number of gaps may exist in your comprehension and use of pressure. Because effective use of pressure is important in chemical engineering practice, this chapter is designed to fill these gaps.

Looking Ahead

In this chapter we review various measures of pressure, both relative and absolute, discuss methods of measuring pressure, and illustrate converting from one set of pressure units to another.

5.1 Pressure and Its Units

In Florentine Italy in the seventeenth century, well diggers observed that, in suction pumps, water would not rise more than about 10 meters. In 1642 they came to the famous Galileo for help, but he did not want to be bothered. As an alternate, they sought the help of Toricelli. He learned from experiments that water was not being pulled up by the vacuum, but rather was being pushed up by the local air pressure.

Pressure is defined as “the normal (perpendicular) force per unit area.” Examine Figure 5.1. Pressure is exerted on the top of the cylinder of mercury by the atmosphere, and on the bottom of the cylinder itself by the mercury, including the effect of the atmosphere.

The pressure at the bottom of the **static** (nonmoving) column of mercury exerted on the sealing plate is

$$p = \frac{F}{A} = \rho gh + p_0 \quad (5.1)$$

where p = pressure at the bottom of the column of the fluid

F = force

A = area

ρ = density of fluid

g = acceleration of gravity

h = height of the fluid column

p_0 = pressure at the top of the column of fluid

In the SI system the force is expressed in newtons, and area in square meters; then the pressure is N/m^2 or pascal (Pa). The value of the Pa is so small that the kilopascal (kPa) is a more convenient unit of pressure.

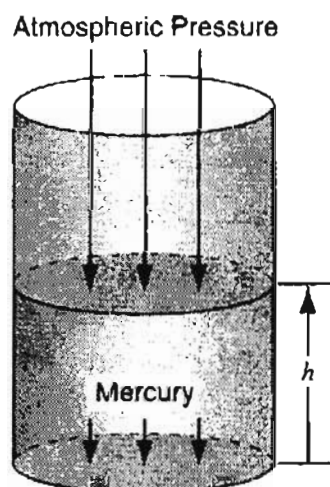


Figure 5.1 Pressure is the normal force per unit area. Arrows show the force exerted on the respective areas.

Some common nonstandard variations of pressure measurement used with the SI system are

- a. Bars (bar): $100 \text{ kPa} = 1 \text{ bar}$
- b. Kilograms (force) per square centimeter (kg_f/cm^2)*—a very common measure of pressure but not standard in SI (often called just “kilos”)
- c. Torr (Torr): $760 \text{ Torr} = 1 \text{ atm}$

In the AE system pressure can be expressed in a variety of ways, including

- a. Millimeters of mercury (mm Hg)
- b. Inches of mercury (in. Hg)
- c. Feet of water (ft H_2O)
- d. Inches of water (in. H_2O)
- e. Atmospheres (atm)
- f. Pounds (force) per square inch (often called just “pounds”) (psi)

Keep in mind the confusion that can be caused by the nontechnical use of the word “pounds,” such as the caption on a cartoon that read

“It says inflate to 12 pounds. How can I throw a 12-pound football?”

You can calculate the force exerted at the bottom of a *static* fluid by applying Equation (5.1). For example, suppose that the cylinder of fluid in Figure 5.1 is a column of mercury that has an area of 1 cm^2 and is 50 cm high. From Table D1 in the Appendix you can find the specific gravity of mercury at 20°C , and hence the density of the Hg, is 13.55 g/cm^3 . Thus, the force exerted by the mercury alone on the 1-cm^2 section of the bottom plate by the column of mercury is

$$F = \frac{13.55 \text{ g}}{\text{cm}^3} \left| \frac{980 \text{ cm}}{\text{s}^2} \right| \left| \frac{50 \text{ cm}}{1} \right| \left| \frac{1 \text{ cm}^2}{1} \right| \left| \frac{1 \text{ kg}}{1000 \text{ g}} \right| \left| \frac{1 \text{ m}}{100 \text{ cm}} \right| \left| \frac{1(\text{N})(\text{s}^2)}{1(\text{kg})(\text{m})} \right|$$

$$= 6.64 \text{ N}$$

The pressure on the section of the plate covered by the mercury is the force per unit area of the mercury *plus* the pressure of the atmosphere

$$p = \frac{6.64 \text{ N}}{1 \text{ cm}^2} \left| \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 \right| \left| \frac{(1 \text{ m}^2)(1 \text{ Pa})}{(1 \text{ N})} \right| \left| \frac{1 \text{ kPa}}{1000 \text{ Pa}} \right| + p_0 = 66.4 \text{ kPa} + p_0$$

*Although the units of pressure in the SI system are pascal, in common usage pressures are frequently denoted in the units of kg/cm^2 (i.e., kg_f/cm^2), units that have to be multiplied by

$$9.80 \times 10^4 \left(\frac{(\text{kg}_m)(\text{m})}{(\text{kg}_f)(\text{s}^2)} \right) \left(\frac{\text{cm}^2}{\text{m}^2} \right) \text{ to get pascal}$$

If we had started with units in the AE system, the pressure would be computed as [the density of mercury is $(13.55)(62.4)\text{lb}_m/\text{ft}^3 = 845.5\text{lb}_m/\text{ft}^3$]

$$p = \frac{845.5\text{ lb}_m}{1\text{ ft}^3} \left| \frac{32.2\text{ ft}}{\text{s}^2} \right| \left| \frac{50\text{ cm}}{1\text{ in.}} \right| \left| \frac{1\text{ in.}}{2.54\text{ cm}} \right| \left| \frac{1\text{ ft}}{12\text{ in.}} \right| \left| \frac{(\text{s})^2(\text{lb}_f)}{32.174(\text{ft})(\text{lb}_m)} \right| + p_0$$

$$= 1388 \frac{\text{lb}_f}{\text{ft}^2} + p_0$$

Sometimes in engineering practice, a liquid column is referred to as *head of liquid*, the head being the height of the column of liquid. Thus, the pressure of the column of mercury could be expressed simply as 50 cm Hg, and the pressure on the sealing plate at the bottom of the column would be 50 cm Hg + p_0 (in cm of Hg).

SELF-ASSESSMENT TEST

Questions

- Figure SAT5.1Q1 shows two coffee pots sitting on a level table. Both are cylindrical and have the same cross-sectional area. Which coffee pot will hold the most coffee?

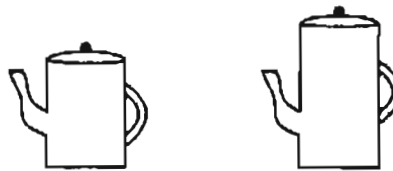


Figure SAT5.1Q1

- Figure SAT5.1Q2 shows four closed containers completely filled with water. Order the containers from the one exerting the highest pressure to the lowest on their respective bases.

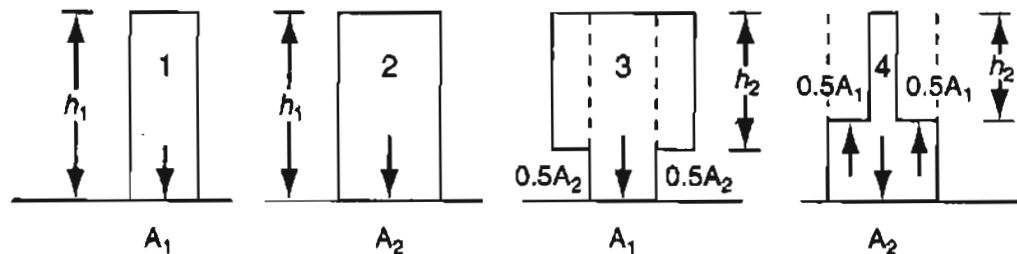


Figure SAT5.1Q2

Thought Problems

- When you lie motionless on a bed, the bed supports you with a force that exactly matches your weight, and when you do the same on the floor, the floor pushes up against you with the same amount of force. Why does the bed feel softer than the floor?

2. If you push the tube shown in Figure TP5.1P2 into the glass of water so that bend A is below the water level, the tube will become a siphon, and drain the water out of the glass. Why does that happen?

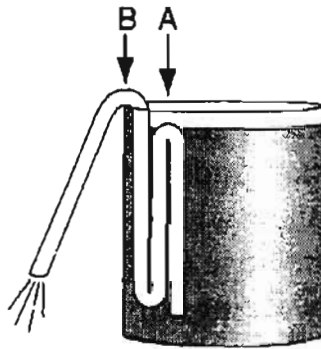


Figure TP5.1P2

5.2 Measurement of Pressure

Pressure, like temperature, can be expressed using either an absolute or a relative scale. **Whether relative or absolute pressure is measured in a pressure-measuring device depends on the nature of the instrument used to make the measurements.** For example, an open-end manometer (Figure 5.2a) would measure a **relative (gauge) pressure**, since the reference for the open end is the pressure of the atmosphere at the open end of the manometer. On the other hand, closing off

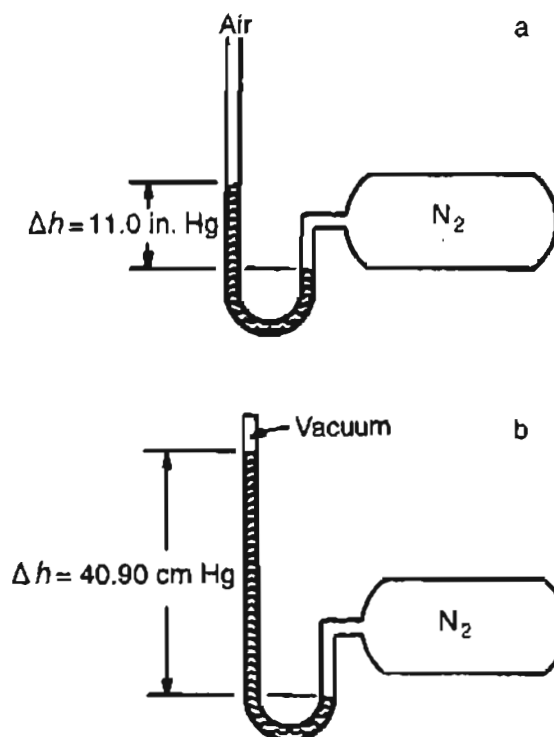


Figure 5.2 (a) Open-end manometer showing a pressure above atmospheric pressure. (b) Manometer measuring an absolute pressure.

the open end of the manometer (Figure 5.2b) and creating a vacuum in that end results in a measurement against a complete vacuum, or against “no pressure”; p_0 in Equation (5.1) is zero. Such a measurement is called **absolute pressure**. Since absolute pressure is based on a complete vacuum, a fixed reference point that is unchanged regardless of location, temperature, weather, or other factors, absolute pressure establishes a precise, invariable value that can be readily identified. In contrast the zero point for a relative or gauge pressure measurement usually corresponds to the pressure of the air that surrounds us at all times, and as you know, varies slightly.

You are probably familiar with the barometer illustrated in Figure 5.3. Does a barometer read absolute or relative (gauge) pressure?

Figure 5.4 shows the workings of a dial device that measures pressure called a **Bourdon gauge**. Does it measure absolute or relative pressure?

A Bourdon gauge normally measures relative pressure, but not always. The pressure-sensing device in the Bourdon gauge is a thin metal tube with an elliptical cross-section closed at one end that has been bent into an arc. As the pressure increases at the open end of the tube, it tries to straighten out, and the movement of the tube is converted into a dial movement by gears and levers.

In any of the pressure-measuring devices depicted in Figures 5.2 to 5.4, the fluid is at equilibrium, meaning that a state of hydrostatic balance is reached stabilizing the manometer fluid. The pressure exerted at the part of the tube open to the atmosphere or vacuum exactly balances the pressure exerted at the other end of the

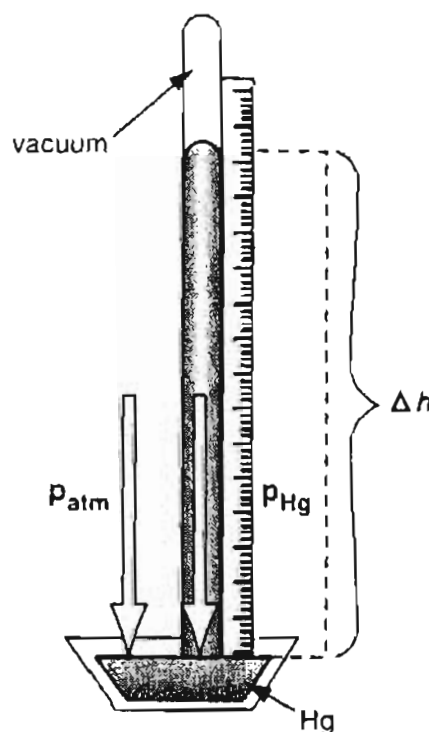


Figure 5.3 A mercury barometer.

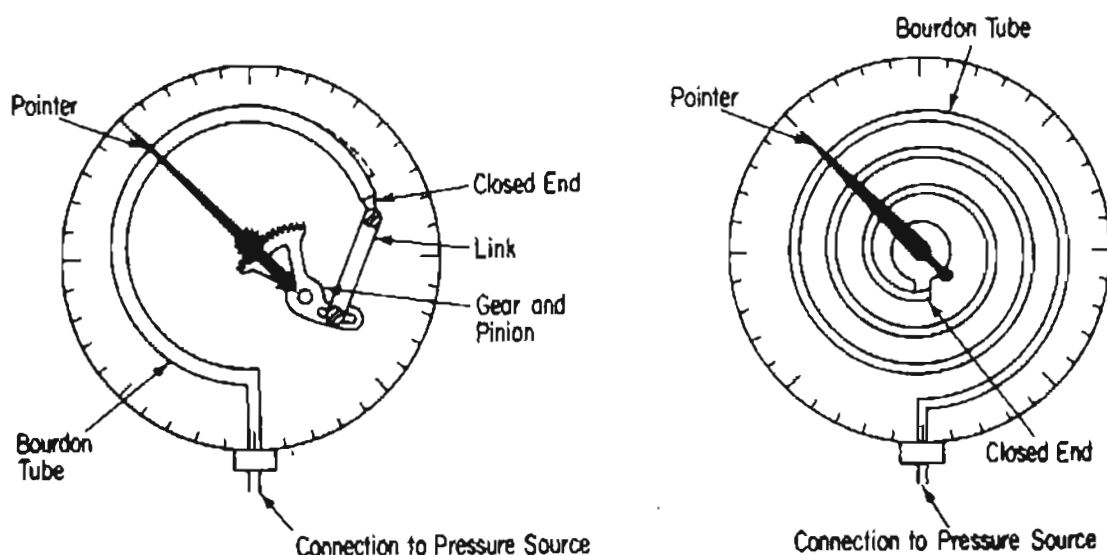


Figure 5.4 Bourdon gauge pressure-measuring devices: (a) "C" Bourdon and (b) Spiral Bourdon.

tube. Water and mercury are commonly used indicating fluids for manometers; the readings thus can be expressed in "inches or cm of water," "inches or cm of mercury," and so on. In ordinary engineering calculations involving pressure we ignore the vapor pressure of mercury (or water) and minor changes in the density of mercury (or water) due to temperature changes.

What are some other examples of pressure-measuring devices? Figure 5.5 presents the names of some common instruments along with their useful ranges.

Another term with which you should become familiar is **vacuum**. In effect, when you measure the pressure in "inches of mercury vacuum," you are reversing the usual direction of measurement, and measure from the atmospheric pressure downward to zero absolute pressure. Thus: *inches Hg vacuum = barometric pressure - absolute pressure*. A pressure-sensing device for vacuum systems is commonly used in an apparatus that operates at pressures less than atmospheric, such as a vacuum filter. A pressure that is only slightly below barometric pressure may sometimes be expressed as a "draft" in inches of water, as, for example, in the air supply to a furnace or a water cooling tower.

Here is a news article (R.E. Sanders, *Chemical Engineering Progress*, September 1993, p. 54) that pertains to Figure 5.6.

Don't Become Another Victim of Vacuum

Tanks are fragile. An egg can withstand more pressure than a tank. How was a vacuum created inside the vessel? As water was drained from the column, the vent to let in air was plugged up, and the resulting pressure difference between inside and out caused the stripper to fail.

We can conclude: don't let your vacuum get you down!

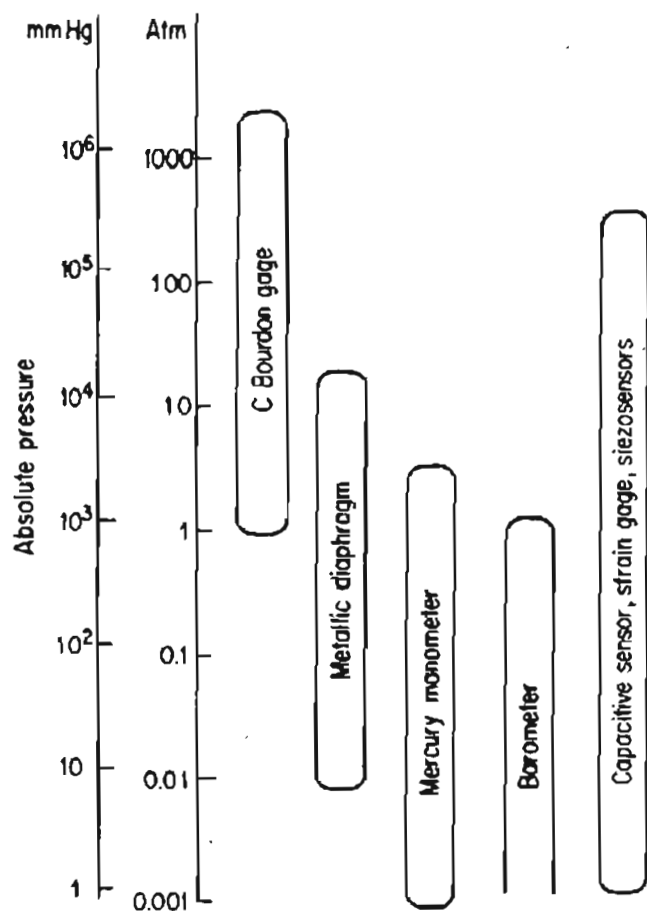


Figure 5.5 Ranges of application for pressure-measuring devices.

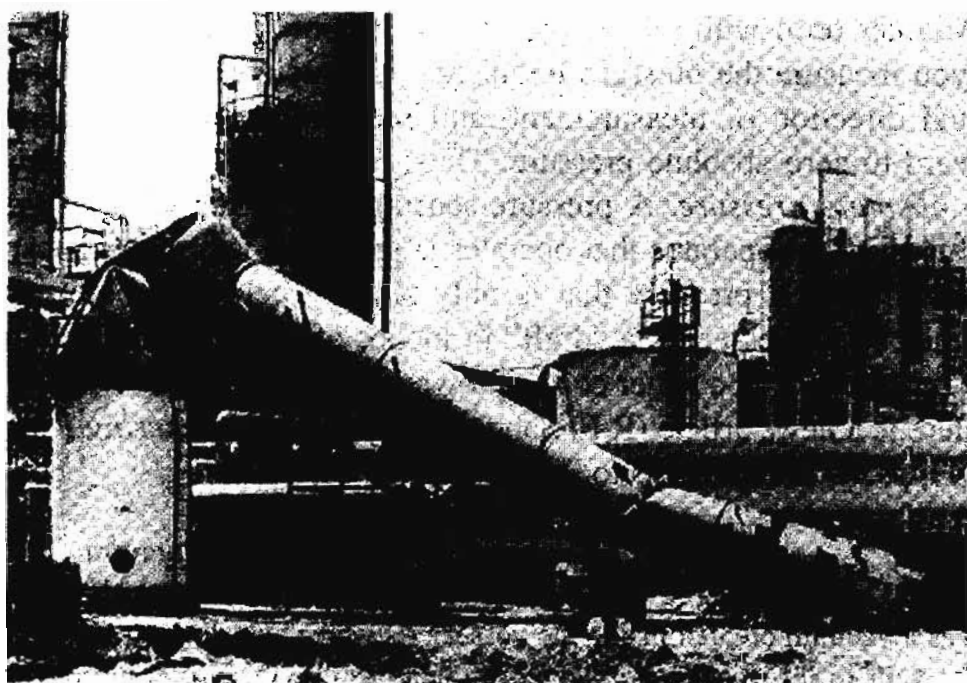


Figure 5.6 Close-up of a failed stripper column (Reproduced through the courtesy of Roy E. Sanders).

Always keep in mind that the reference point or zero point for the relative pressure scales or for a vacuum scale is not constant, and that the relationship between relative and absolute pressure is given by the following expression:

$$\text{gauge pressure} + \text{barometer pressure} = \text{absolute pressure} \quad (5.2)$$

Examine Figure 5.7.

You definitely must not confuse the standard atmosphere with atmospheric pressure. The standard atmosphere is defined as the pressure (in a standard gravitational field) equivalent to 1 atm or 760 mm Hg at 0°C or other equivalent value, whereas atmospheric pressure is variable and must be obtained from a barometric measurement each time you need it. Look at Figure 5.7 for clarification.

The standard atmosphere may not equal the barometric pressure in any part of the world except perhaps at sea level on certain days. However, it is extremely useful converting from one system of pressure measurement to another (as well as being useful in several other ways, to be considered in Chapter 13). In a problem, if you are not given the barometric pressure, you usually *assume* that the barometric pressure equals the standard atmosphere, but this assumption is only that—an assumption.

Expressed in various units, the **standard atmosphere** is equal to

1.000 atmospheres (atm)

33.91 feet of water (ft H₂O)

14.7 (14.696, more exactly) pounds (force) per square inch absolute (psia)

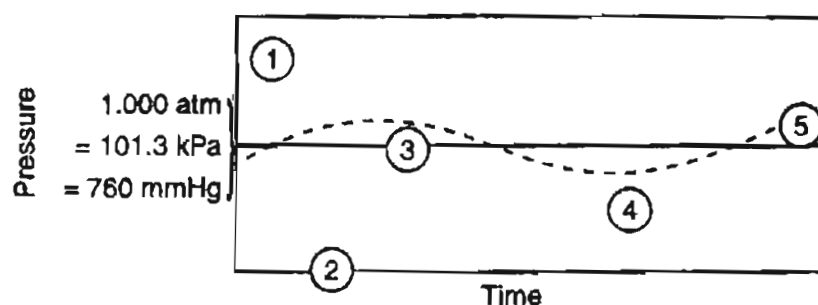


Figure 5.7 Pressure terminology. Note that the vertical scale is exaggerated for illustrative purposes. The dashed line illustrates the atmospheric (barometric) pressure, which changes from time to time. Point ① in the figure denotes a pressure of 19.3 psia, that is, a pressure referred to a complete vacuum, or 5 psi referred to the barometric pressure, ② is the complete vacuum or zero pressure, any point on the heavy line such as ③ is a point corresponding to the standard pressure, and ④ illustrates a negative relative pressure, that is, a pressure less than atmospheric pressure. This latter type of measurement is described in the text as a vacuum measurement. Point ⑤ also indicates a vacuum measurement, but one that is equivalent to an absolute pressure above the standard atmosphere.

29.92 (29.921, more exactly) inches of mercury (in. Hg)

760.0 millimeters of mercury (mm Hg)

1.013×10^5 pascal (Pa) or newtons per square meter (N/m^2); or 101.3 kPa

Because the standard atmosphere is an absolute pressure, you can easily convert from one set of pressure units to another by using a pair of standard atmospheres as a conversion factor as follows. We will convert 35 psia to inches of mercury and kPa by using ratios of the standard atmosphere to carry out the conversions:

$$\frac{35 \text{ psia}}{14.7 \text{ psia}} \left| \frac{29.92 \text{ in. Hg}}{14.7 \text{ psia}} \right. = 71.24 \text{ in Hg}$$

$$\frac{35 \text{ psia}}{14.7 \text{ psia}} \left| \frac{101.3 \text{ kPa}}{14.7 \text{ psia}} \right. = 241 \text{ kPa}$$

In summary, look at Figure 5.8, which illustrates the relationships between relative and absolute pressure for two of the AE pressure units and the SI units. Figure 5.8 shows the relations in pounds (force) per square inch (psi), inches of mercury (in. Hg), and pascals. Pounds per square inch absolute is normally abbreviated "psia"; "psig" denotes "pounds per square inch gauge." Sometimes you have to use

	Pounds per square inch		mm mercury		Inches mercury		newtons per square meter		
A pressure above atmospheric	5.0	19.3	259	998	39.3	10.2	0.34×10^5	1.33×10^5	
Standard atmosphere	0.4	14.7	20.7	760	29.92	0.82	0.028×10^5	1.013×10^5	
Barometric pressure	0.0	14.3	0.0	740	29.1	0	0.00	0.985×10^5	
A pressure below atmospheric—2.45	11.85	2.45			24.1	-5.0	-0.17×10^5	0.82×10^5	0.17×10^5
	↑ Gage pressure ↓ Absolute pressure Vacuum		↑ Gage pressure ↓ Absolute pressure Vacuum		↑ Gage pressure ↓ Absolute pressure Vacuum		↑ Gage pressure ↓ Absolute pressure Vacuum		
Perfect vacuum									
	-14.3	0.0	14.3	0	0	-29.1	-0.985×10^5	0.00	0.985×10^5

Figure 5.8 Pressure comparisons when barometer reading is 29.1 in. Hg.

common sense as to which is being measured if the letters psi are used. For other pressure units, be certain to carefully specify whether they are gauge or absolute units, although you rarely find people doing so. For example, state “300 kPa absolute” or “12 cm Hg gauge” rather than just 300 kPa or 12 cm Hg, as the latter two can on occasion cause confusion.

EXAMPLE 5.1 Pressure Conversion

The structures and dislocations in ceramic material determine the strength of the material in nanotechnology. Nonomaterials are more flexible than ordinary composites because each of the nanocrystallites (particles) can move past each other so that stretching can occur. However, nanosized particles can also enhance hardness. Crystallites pack together along the boundaries of macrocrystallites, and prevent the structure from unzipping. For example, a hardness in excess of 60 gigapascals has been reported for nanocrystals of titanium nitride embedded in thin films of silicon nitride. Hardness is measured by the pressure required to just indent the surface of a material (diamonds exhibit a hardness of greater than 100 Gpa).

What is the equivalent pressure to 60 Gpa in

- (a) atmospheres
- (b) psia
- (c) inches of Hg
- (d) mm of Hg

Solution

For the solution, use the standard atmosphere.

Basis: 60 GPa

$$(a) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \left| \frac{1 \text{ atm}}{101.3 \text{ kPa}} \right| = 0.59 \times 10^6 \text{ atm}$$

$$(b) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \left| \frac{14.696 \text{ psia}}{101.3 \text{ kPa}} \right| = 8.70 \times 10^6 \text{ psia}$$

$$(c) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \left| \frac{29.92 \text{ in. Hg}}{101.3 \text{ kPa}} \right| = 1.77 \times 10^7 \text{ in. Hg}$$

$$(d) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \left| \frac{760 \text{ mm Hg}}{101.3 \text{ kPa}} \right| = 4.50 \times 10^8 \text{ mm Hg}$$

EXAMPLE 5.2 Pressure Conversion

The pressure gauge on a tank of CO₂ used to fill soda-water bottles reads 51.0 psi. At the same time the barometer reads 28.0 in. Hg. What is the absolute pressure in the tank in psia? See Figure E5.2.

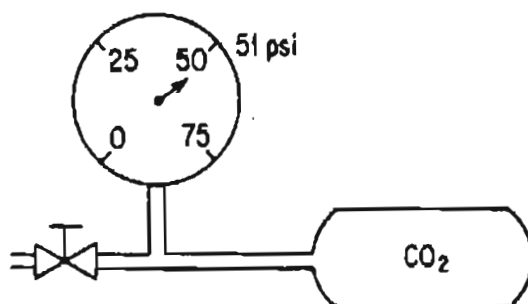


Figure E5.2

Solution

The first thing to do is to read the problem. You want to calculate a pressure using convenient conversion factors, namely the standard atmosphere.

Then examine Figure E5.2. The system is the tank plus the line to the gauge. All of the necessary data are known except what psi means. Is the pressure gauge reading psig, not psia? Yes. You can assume the gauge is a Bourdon gauge measuring relative pressure. Equation (5.2) states that the absolute pressure is the sum of the gauge pressure and the atmospheric (barometric) pressure expressed in the same units. Let us change the atmospheric pressure to psia.

The calculation is

$$\text{Atmospheric pressure} = \frac{28.0 \text{ in. Hg}}{29.92 \text{ in Hg}} \left| \frac{14.7 \text{ psia}}{1} \right. = 13.76 \text{ psia}$$

The absolute pressure in the tank is

$$51.0 \text{ psia} + 13.76 \text{ psia} = 64.8 \text{ psia}$$

Lastly, you always need to check your answers. Try using a different conversion factor. You might first convert the barometric pressure to atm, then the gauge reading to atm, add the pressure in atm, and finally convert the result to psia. A long way to solve the problem, of course, but try it.

EXAMPLE 5.3 Vacuum Pressure Reading

Small animals such as mice can live (although not comfortably) at reduced air pressures down to 20 kPa absolute. In a test, a mercury manometer attached to a tank, as shown in Figure E5.3, reads 64.5 cm Hg and the barometer reads 100 kPa. Will the mice survive?

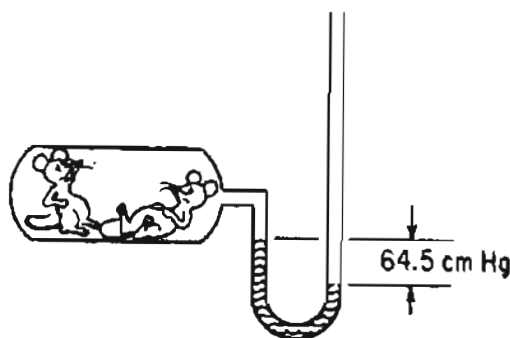


Figure E5.3

Solution

First read the problem. You are expected to realize from the figure that the tank is below atmospheric pressure because the left leg of the manometer is higher than the right leg, which is open to the atmosphere. Consequently, to get the absolute pressure you subtract the 64.5 cm Hg from the barometer reading.

We ignore any corrections to the mercury density for temperature, and also ignore the gas density above the manometer fluid because it is much lower than the density of mercury. Then, since the vacuum reading on the tank is 64.5 cm Hg below atmospheric, the absolute pressure in the tank is

$$100 \text{ kPa} - \frac{64.5 \text{ cm Hg}}{76.0 \text{ cm Hg}} \left| \frac{101.3 \text{ kPa}}{76.0 \text{ cm Hg}} \right| = 100 - 86 = 14 \text{ kPa absolute}$$

The mice probably will not survive.

SELF-ASSESSMENT TEST**Questions**

1. Answer the following questions true or false:
 - a. Atmospheric pressure is the pressure of the air surrounding us and changes from day to day.
 - b. The standard atmosphere is a constant reference atmosphere equal to 1.000 atm or the equivalent pressure in other units.

- c. Absolute pressure is measured relative to a vacuum.
 - d. Gauge pressure is measured upward relative to atmospheric pressure.
 - e. Vacuum and draft pressures are measured downward from atmospheric pressure.
 - f. You can convert from one type of pressure measurement to another using the standard atmosphere.
 - g. A manometer measures the pressure difference in terms of the height of fluid(s) in the manometer tube.
2. What is the equation to convert gauge pressure to absolute pressure?
 3. What are the values and units of the standard atmosphere for six different methods of expressing pressure?
 4. What is the equation to convert vacuum pressure to absolute pressure?

Problems

1. Convert a pressure of 800 mm Hg to the following units:
 - a. psia
 - b. kPa
 - c. atm
 - d. ft H₂O
2. Your textbook lists five types of pressures: atmospheric pressure, barometric pressure, gauge pressure, absolute pressure, and vacuum pressure.
 - a. What kind of pressure is measured by the device in Figure SAT5.2P2A?

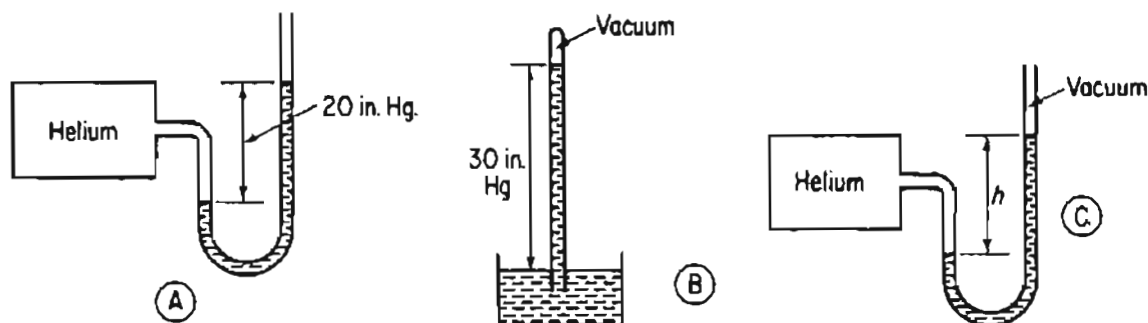


Figure SAT5.2P2A

- b. What kind of pressure is measured by the device in Figure SAT5.2P2B?
- c. What would be the reading in Figure SAT5.2P2C assuming that the pressure and temperature inside and outside the helium tank are the same as in parts (a) and (b)?
3. An evaporator shows a reading of 40 kPa vacuum. What is the absolute pressure in the evaporator in kPa?

Thought Problems

1. A magic trick is to fill a glass with water, place a piece of paper over the top of the glass to cover the glass completely, and hold the paper in place as the glass is inverted 180°. On the release of your support of the paper, no water runs out! Many books state that the

glass should be completely filled with water with no air bubbles present. Then the outside air pressure is said to oppose the weight of the water in the inverted glass. However, the experiment works just as well with a half-filled glass. The trick does not work if a glass plate is substituted for the piece of paper. Can you explain why?

2. A large storage tank was half full of a flammable liquid quite soluble in water. The tank needed maintenance on the roof. Since welding was involved, the foreman attached a flexible hose to the vent pipe on the top of the tank (in which there was a flame arrestor), and inserted the end of the hose into the bottom of a drum of water sitting on the ground to pick up any exhaust vapors. When the tank was emptied, the water rose up in the hose, and the tank walls collapsed inward.

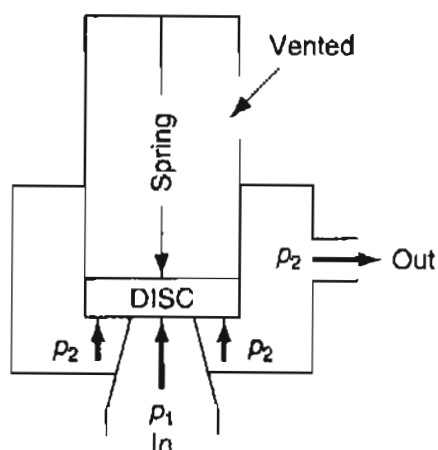
What went wrong in this incident?

3. Can a pressure lower than a complete vacuum exist?
4. If you fill a Styrofoam™ cup with water, and put a hole in the side, water starts to run out. However, if you hold your finger over the hole and then drop the cup from a height, water does not run out. Why?

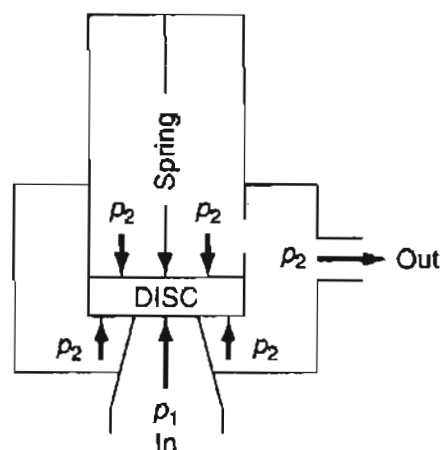
Discussion Problems

1. Safety relief valves protect against excessive pressure in pipelines and process equipment. Excessive pressure can occur because of equipment failure in the process, fire, or human error. A valve of the proper size must be selected for anticipated scenarios, and the spring set for the proper relief pressure.

Two different valves (A and B) are proposed for use in a pipeline, as illustrated in Figure DP5.2P1. Which valve would you recommend for use?



(A) This valve has the top of the closing disk open to the outlet (p_2)



(B) This valve has the top and bottom of the closing disk open to the outlet (p_2)

Figure DP5.2P1

2. Form a study group to investigate the possibility of raising the *Titanic*. The mystique of the sinking and attempts to raise the vessel have crept into the literature (*A Night to Remember*), the movie ("Raising the Titanic"), and magazines such as *National Geographic*.

Carry out a literature search to get the basic facts (4000 m deep, 4.86×10^8 N original weight, the density of sea water, and so on).

Prepare a report giving:

- An executive summary including an estimate of feasibility.
- The proposed method(s) of raising the ship.
- A list of steps to execute to raise the ship.
- A list of the equipment needed (include costs if possible).
- A time schedule for the entire project (including obtaining the equipment and personnel).
- A list of (1) all assumptions made and (2) problems that might be encountered for which answers are not known.
- As an appendix, show all calculations made and references used.

5.3 Differential Pressure Measurements

Have you noted in the discussion and examples so far that we have ignored the gas in the manometer tube above the fluid. Is this OK? Let's see. Examine Figure 5.9, which illustrates a manometer involving three fluids.

When the columns of fluids are at equilibrium (it may take some time!), the relationship among ρ_1 , ρ_2 , ρ_3 , and the heights of the various columns of fluid is as follows. Pick a reference level for measuring pressure at the bottom of d_1 . (If you pick the very bottom of the U tube instead of d_1 as the reference, the lefthand and righthand distances up to d_1 are equal, and, consequently, the pressures exerted by the righthand and lefthand legs of the U-tube will cancel out in Equation (5.3)—try it and see).

$$p_1 + \rho_1 d_1 g = p_2 + \rho_2 g d_2 + \rho_3 g d_3 \quad (5.3)$$

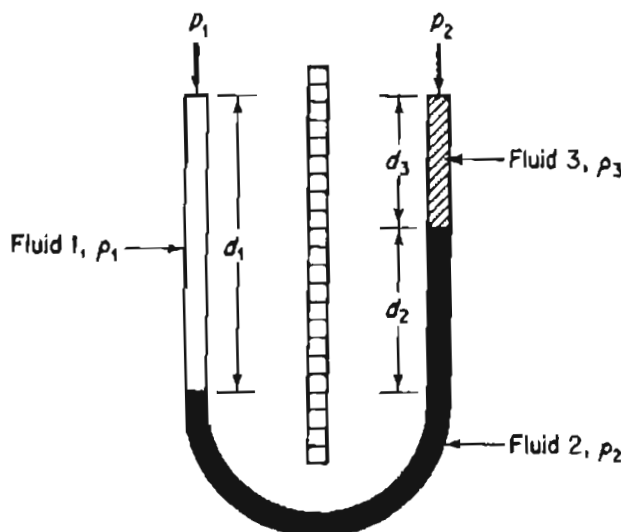


Figure 5.9 Manometer with three fluids.

If fluids 1 and 3 are gases, and fluid 2 is mercury, the density of the gas is so much less than that of mercury that you can ignore the term involving the gas in Equation (5.3) for practical applications.

However, if fluids 1 and 3 are liquids and fluid 2 is an immiscible fluid, the terms involving the densities of fluids 1 and 3 cannot be neglected in Equation (5.3). As the densities of fluids 1 and 3 approach that of fluid 2, what happens to the differential reading d_2 in Figure 5.9 for a given pressure difference?

Can you show for the case in which $\rho_1 = \rho_3 = \rho$ that the manometer expression reduces to the well-known differential manometer equation?

$$p_1 - p_2 = (\rho_2 - \rho)gd_2 \quad (5.4)$$

As you know, or will learn in Chapter 27, a flowing fluid experiences a pressure drop when it passes through a restriction such as the orifice in a pipe, as shown in Figure 5.10.

The pressure difference can be measured with any instrument, such as a manometer, connected to the pressure taps, as illustrated in Figure 5.10. Note that the manometer fluid is static if the flow rate in the pipe is constant.

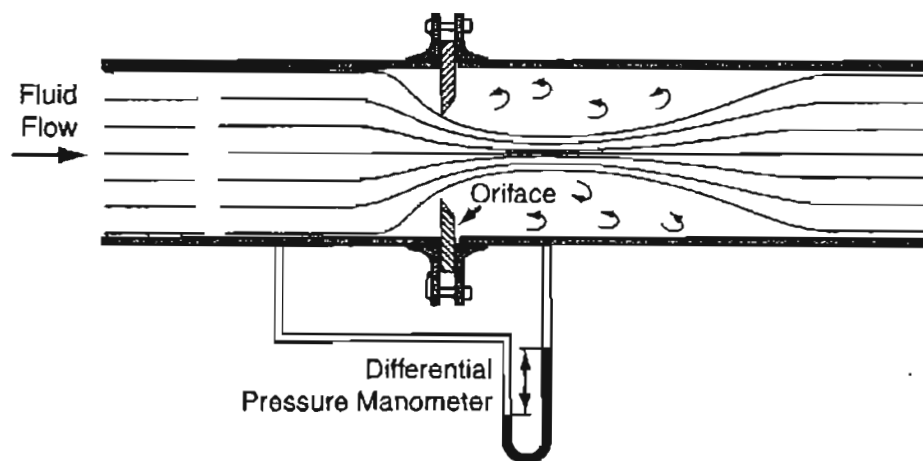


Figure 5.10 Concentric orifice used to restrict flow and measure the fluid flow rate with the aid of a manometer.

EXAMPLE 5.4 Calculation of Pressure Differences

In measuring the flow of fluid in a pipeline as shown in Figure E5.4, a differential manometer was used to determine the pressure difference across the orifice plate.

The flow rate was to be calibrated with the observed pressure drop (difference). Calculate the pressure drop $p_1 - p_2$ in pascals for the manometer reading in Figure E5.4.

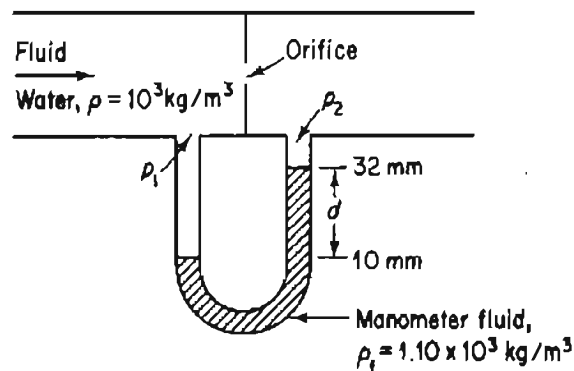


Figure E5.4

Solution

In this problem you cannot ignore the water density above the manometer fluid. Thus, we apply Equation (5.3) or (5.4), because the densities of the fluids above the manometer fluid are the same in both legs of the manometer. The basis for solving the problem is the information given in Figure E5.4. Apply Equation (5.4)

$$\begin{aligned}
 p_1 - p_2 &= (\rho_f - \rho)gd \\
 &= \frac{(1.10 - 1.00)10^3 \text{ kg}}{\text{m}^3} \left| \frac{9.807 \text{ m}}{\text{s}^2} \right| \frac{(22)(10^{-3})\text{m}}{1} \left| \frac{1(\text{N})(\text{s}^2)}{(\text{kg})(\text{m})} \right| \frac{1(\text{Pa})(\text{m}^2)}{1(\text{N})} \\
 &= 21.6 \text{ Pa}
 \end{aligned}$$

Check your answer. How much error would occur if you ignored the density of the flowing fluid?

EXAMPLE 5.5 Pressure Conversion

Air is flowing through a duct under a draft of 4.0 cm H₂O. The barometer indicates that the atmospheric pressure is 730 mm Hg. What is the absolute pressure of the air in inches of mercury? See Figure E5.5

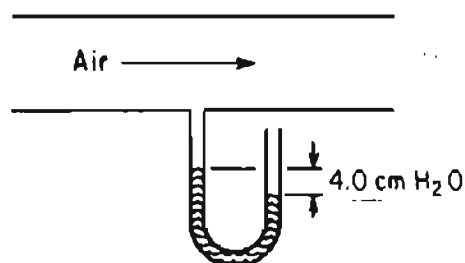


Figure E5.5

Solution

Can you ignore the gas density above the manometer fluid and the air above the open end of the manometer? Probably. In the calculations you must employ consistent units, and it appears in this case that the most convenient units are those of inches of mercury, so let's convert the barometer reading and the manometer reading to in. Hg using the standard atmosphere as the conversion factor.

$$\text{Atmospheric pressure} = \frac{730 \text{ mm Hg}}{760 \text{ mm Hg}} \left| \frac{29.92 \text{ in. Hg}}{1} \right| = 28.7 \text{ in. Hg}$$

Next, convert 4.0 cm H₂O to in. Hg:

$$\frac{4.0 \text{ cm H}_2\text{O}}{2.54 \text{ cm}} \left| \frac{1 \text{ in.}}{1} \right| \left| \frac{1 \text{ ft}}{12 \text{ in.}} \right| \left| \frac{29.92 \text{ in. Hg}}{33.91 \text{ ft H}_2\text{O}} \right| = 0.12 \text{ in. Hg}$$

Since the reading is 4.0 cm H₂O draft (under atmospheric), the absolute reading in uniform units is

$$28.7 \text{ in. Hg} - 0.12 \text{ in. Hg} = 28.6 \text{ in. Hg absolute}$$

SELF-ASSESSMENT TEST**Questions**

1. Answer the following questions true or false:
 - a. Air flows in a pipeline. A manometer containing Hg is set up as illustrated in Figure E5.4, and shows a differential pressure of 14.2 mm Hg. You can ignore the effect of the density of air on the height of the columns of mercury.
 - b. Lowering the He pressure in Figure SAT5.2P2A (see the SAT problems in Section 5.2) will not cause the length of the column of Hg to decrease by 10%.

Problems

1. A U-tube manometer filled with mercury is connected between two points in a pipeline. If the manometer reading is 26 mm of Hg, calculate the pressure difference in kPa between the points when (a) water is flowing through the pipeline, and (b) also when air at atmospheric pressure and 20°C with a density of 1.20 kg/m³ is flowing in the pipeline.
2. A Bourdon gauge and a mercury manometer are connected to a tank of gas, as shown in Figure SAT5.3P2. If the reading on the pressure gauge is 85 kPa, what is h in centimeters of Hg?

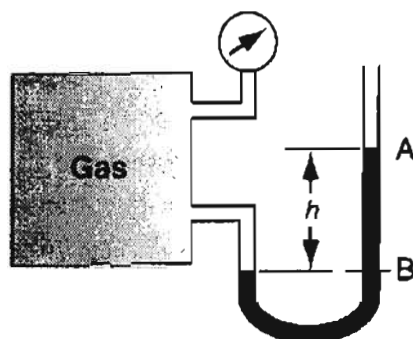


Figure SAT5.3P2

Looking Back

In this chapter we defined pressure, discussed some of the common ways to measure pressure, and showed how to convert from one set of pressure units to another by using the standard atmosphere. We also emphasized the difference between the standard atmosphere and atmospheric pressure.

GLOSSARY OF NEW WORDS

Absolute pressure Pressure relative to a complete vacuum.

Barometric pressure Absolute pressure measure measured by a barometer.

Bourdon gauge Pressure measuring device containing a thin metal tube that flexes and moves a dial as the pressure being measured changes.

Gauge pressure Pressure measured above atmospheric pressure.

Manometer A U-tube or other device containing a fluid that moves in the tube as the pressure difference across the sides of the tube changes. The difference in the height of the fluid in the two sides of the tube indicates the pressure difference.

Pressure The normal force per unit area that a fluid exerts on a surface.

Pressure difference The difference between the pressure at one point and another, usually as measured by an instrument.

Relative pressure Same as gauge pressure.

Standard atmosphere The pressure in a standard gravitational field equivalent to 760 (exactly) mm Hg.

Vacuum A pressure less than atmospheric (but reported as a positive number).

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the FAQ in the front material, the following are pertinent.

- American Society of Heating, Refrigeration, and Air Conditioning Engineers. *Standard Method for Pressure Measurement* (Ashrae Standards No. 41.3), Ashrae (1989).
- Benedict, R. P. *Fundamentals of Temperature, Pressure, and Flow Measurement*, 3rd ed., John Wiley, New York (1984)
- Cengel, Y. A., and M. A. Boles. *Thermodynamics*, 4th ed., McGraw-Hill, New York (2002).
- Gillum, D. R. *Industrial Pressure, Level, and Density Measurement*. Instrumentation, Systems, and Automation Society (1995).

Web Sites

- <http://thermal.sdsu.edu/testcenter/Test/solve/basics/pressure/pressure.html>
- <http://www.efm.leeds.ac.uk/CIVE/CIVE1400/Section2/Manometers.html>
- <http://www.mas.ncl.ac.uk/~sbrooks/nish.mit.edu/2006/Textbook/Nodes/chapo2/node9.html>
- <http://www.omega.com/literature/transactions/volume3/pressure.html>

PROBLEMS

*5.1 From the newspaper:

“BROWNSVILLE, TX. Lightning or excessive standing water on the roof of a clothes store are emerging as the leading causes suspected in the building’s collapse. Mayor Ignacio Garza said early possibilities include excessive weight caused by standing water on the 19-year-old building’s roof. Up to six inches of rain fell here in less than six hours.”

Flat-roof buildings are a popular architectural style in dry climates because of the economy of materials of construction. However, during the rainy season water may pool up on the roof decks so that structural considerations for the added weight must be taken into account. If 15 cm of water accumulates on a 10-m by 10-m area during a heavy rain storm, determine:

- (a) The total added weight the building must support.
- (b) The force of the water on the roof in psi.

- **5.2** A problem with concrete wastewater treatment tanks set below ground was realized when the water table rose and an empty tank floated out of the ground. This buoyancy problem was overcome by installing a check valve in the wall of the tank so that if the water table rose high enough to float the tank, it would fill with water. If the density of concrete is 2080 kg/m^3 , determine the maximum height at which the valve should be installed to prevent a buoyant force from raising a rectangular tank with inside dimensions of 30 m by 27 m and 5 m deep. The walls and floor have a uniform thickness of 200 mm.

- *5.3 A centrifugal pump is to be used to pump water from a lake to a storage tank that is 148 ft above the surface of the lake. The pumping rate is to be 25.0 gal/min, and the water temperature is 60°F. The pump on hand can develop a pressure of 50.0 psig when it is pumping at a rate of 25.0 gal/min. (Neglect pipe friction, kinetic energy effects, or factors involving pump efficiency.)
 (a) How high (in feet) can the pump raise the water at this flow rate and temperature?
 (b) Is this pump suitable for the intended service?
- *5.4 A manometer uses kerosene, sp gr 0.82, as the fluid. A reading of 5 in. on the manometer is equivalent to how many millimeters of mercury?
- *5.5 A manufacturer of large tanks calculates the mass of fluid in the tank by taking the pressure measurement at the bottom of the tank in psig, and then multiplies that value by the area of the tank in square inches. Can this procedure be correct?
- *5.6 A letter to the editor says

“An error in units was made in the article “Designing Airlift Loop Fermenters.” Equation (4) is not correct

$$\Delta p = 4f\rho [(v^2/2g)(L/D)] \quad (4)$$

Is the author of the letter correct? (f is dimensionless.)

- *5.7 Leaking oil tanks have become such environmental problems that the Federal Government has implemented a number of rules to reduce the problem. A leak from a small hole in a tank can be predicted from the following relation:

$$Q = 0.61 S \sqrt{(2\Delta p)\rho}$$

where Q = the leakage rate

S = crosssectional area of the leak

Δp = pressure drop

ρ = fluid density

To test the tank, the vapor space is pressurized with N_2 to a pressure of 23 psig. If the tank is filled with 73 inches of gasoline (sp. gr. = 0.703) and the hole is 1/4 in. in diameter, what is the initial value of Q (in ft³/hr)?

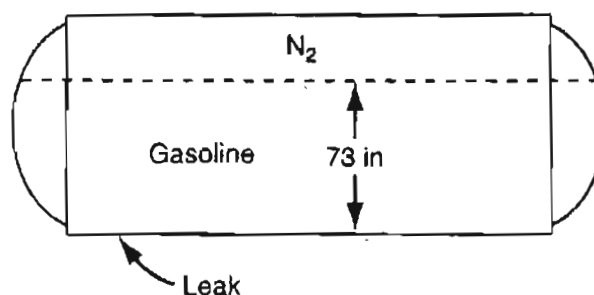


Figure P5.7

- *5.8 Suppose that a submarine inadvertently sinks to the bottom of the ocean at a depth of 1000 m. It is proposed to lower a diving bell to the submarine and attempt to enter the conning tower. What must the minimum air pressure be in the diving bell at the level

of the submarine to prevent water from entering into the bell when the opening valve at the bottom is cracked open slightly? Give your answer in absolute kilopascal. Assume that seawater has a constant density of 1.024 g/cm^3 .

- *5.9 A pressure gauge on a welder's tank gives a reading of 22.4 psig. The barometric pressure is 28.6 in. Hg. Calculate the absolute pressure in the tank in (a) lb_f/ft^2 ; (b) in. Hg; (c) newtons/(meter) 2 ; and (d) ft water.
- *5.10 John Long says he calculated from a formula that the pressure at the top of Pikes Peak is 9.75 psia. John Green says that it is 504 mm Hg because he looked it up in a table. Which John is right?
- **5.11 The floor of a cylindrical water tank was distorted into 7-in. bulges due to the settling of improperly stabilized soil under the tank floor. However, several consulting engineers restored the damaged tank to use by placing plastic skirts around the bottom of the tank wall and devising an air flotation system to move it to an adjacent location. The tank was 30.5 m in diameter and 13.1 m deep.
- The top, bottom, and sides of the tank were made of 9.35-mm-thick welded steel sheets. The density of the steel is 7.86 g/cm^3 .
- (a) What was the gauge pressure in kPa of the water at the bottom of the tank when it was completely full of water?
- (b) What would the air pressure have to be in kPa beneath the empty tank in order to just raise it up for movement?
- *5.12 A pressure instrument has failed on a process line that requires constant monitoring. A bell-type gauge as shown in Figure P5.12 is available that has oil (density of

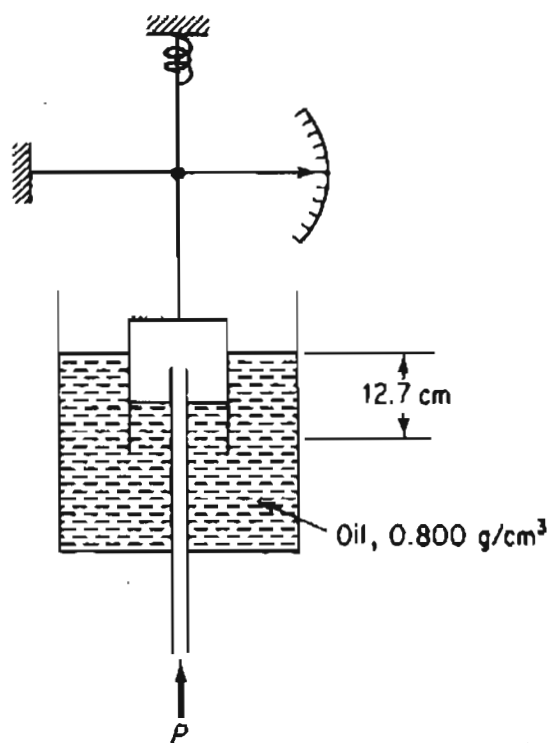


Figure P5.12

0.800 g/cm³) as a sealant liquid. Construction of the gauge limits the sealant liquid's travel to 12.7 cm before blowout of the oil occurs. What maximum pressures can this gauge measure in kPa?

***5.13** A Bourdon pressure gauge is connected to a large tank and reads 440 kPa when the barometer reads 750 mm Hg. What will the gauge reading be if the atmospheric pressure increases to 765 mm Hg?

****5.14** A gauge on a closed tank as shown in the accompanying figure reads 20 pounds per square inch. The contents of the tank are air and a hydrocarbon.

- Does the gage read gage pressure or absolute pressure? State which and why.
- What is the pressure at the bottom of the tank in psia if the specific gravity of the hydrocarbon is 0.92?

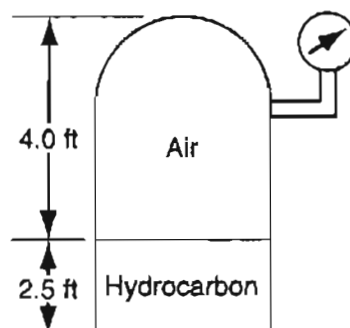


Figure P5.14

****5.15** A gas cylinder to which is attached an Bourdon gage appears to be at a pressure of 27.38 in. Hg at 70°F; the barometer reads 101.8 kPa. A student claims that the pressure in the tank is 1.3 psia, but another student points out that this is impossible—the pressure is really 28.2 psia. Can 1.3 psia be correct? Explain and show calculations to back up your explanation.

***5.16** The pressure gauge on the steam condenser for a turbine indicates 26.2 in. Hg of vacuum. The barometer reading is 30.4 in. Hg. What is the absolute pressure in the condenser in psia?

***5.17** A pressure gauge on a process tower indicates a vacuum of 3.53 in. Hg. The barometer reads 29.31 in. Hg. What is the absolute pressure in the tower in millimeters of mercury?

*****5.18** A student connected a Bourdon gauge designed to read gauge pressure to a vacuum line and, on finding out that it would not give a reading, decided to adjust the instrument so that it read 0 psi for a high vacuum, and read 14.7 psi at atmospheric pressure. However, on the day when this adjustment was made, the barometer read 735 mm Hg, so that his reading of 14.7 psi was slightly in error.

This gauge was later used to measure a pressure in a tank of air, and read 51 psig. What should the proper gauge reading be? The barometer at that time was 750 mm Hg. State any assumptions needed to solve this problem.

***5.19** A vacuum gauge connected to a tank reads 31.5 kPa. What is the corresponding absolute pressure if the barometer reads 98.2 kPa?

- *5.20** Your boss asks you to drain a completely full leak proof water storage tank 12 m high and 3 m in diameter by opening a valve at the bottom of the tank. What response should you give to your boss?
- *5.21** A centrifugal pump is to be used to pump water from a lake to a storage tank which is 148 feet above the surface of the lake. The pumping rate is to be 25.0 gallons per minute, and the water temperature is 60°F.
- The pump on hand can develop a discharge pressure of 50.0 psig when it is pumping at a rate of 25.0 gal/min. (Neglect pipe friction, kinetic energy effects, or factors involving pump efficiency.)
- (a) How high can the pump raise the water at this flow rate and temperature? Give answer in feet.
- (b) Is this pump suitable for the intended service?
- *5.22** Examine Figure P5.22. Oil (density = 0.91 g/cm³) flows in a pipe, and the flow rate is measured via a mercury (density = 13.546 g/cm³) manometer. If the difference in height of the two legs of the manometer is 0.78 in., what is the corresponding pressure difference between points A and B in mm Hg? At which point, A or B, is the pressure higher? The temperature is 60°F.

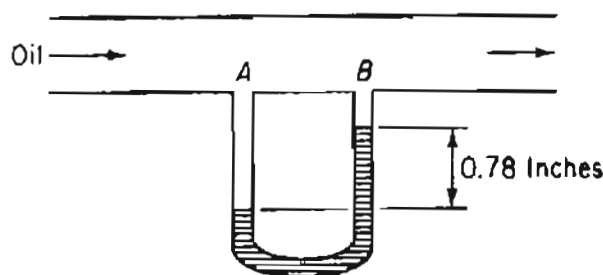


Figure P5.22

- **5.23** Examine Figure P5.23. The barometer reads 740 mm Hg. Calculate the pressure in the tank in psia.

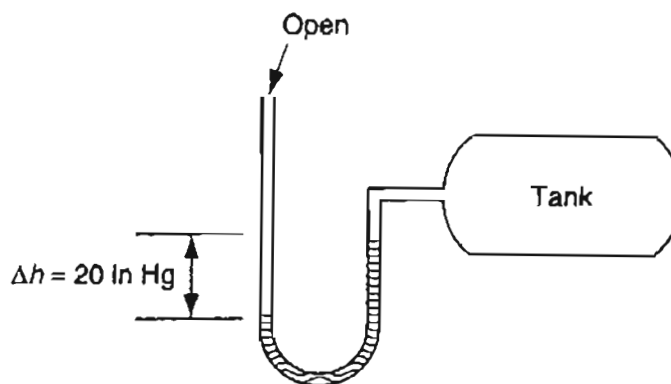


Figure P5.23

- ***5.24** In Figure P5.24, Hg is used to measure the pressure between the points M and N. Water occupies the space above the Hg. What is Δp between M and N? Which pressure is higher, p_M or p_N ?

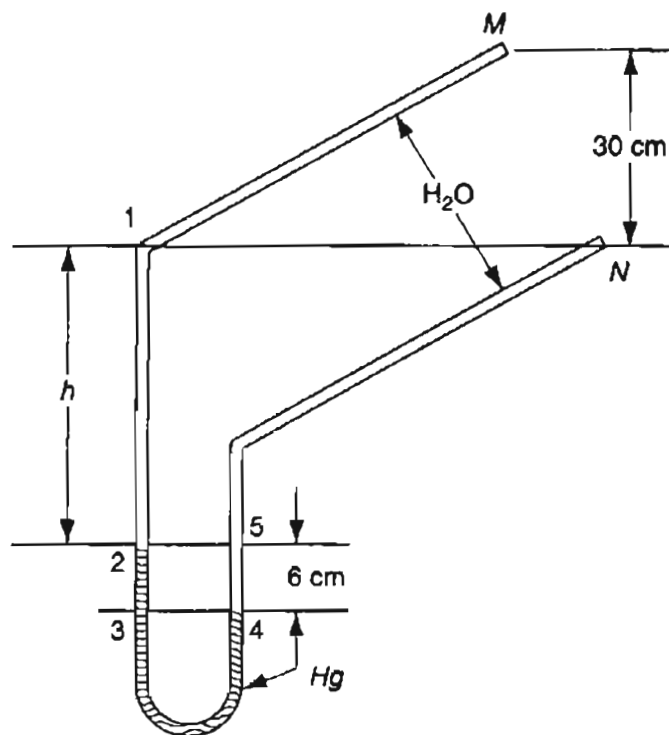


Figure P5.24

5.25 Express p_B as a function of h based on the data given in Figure P5.25. The non-shaded tube contains oil.

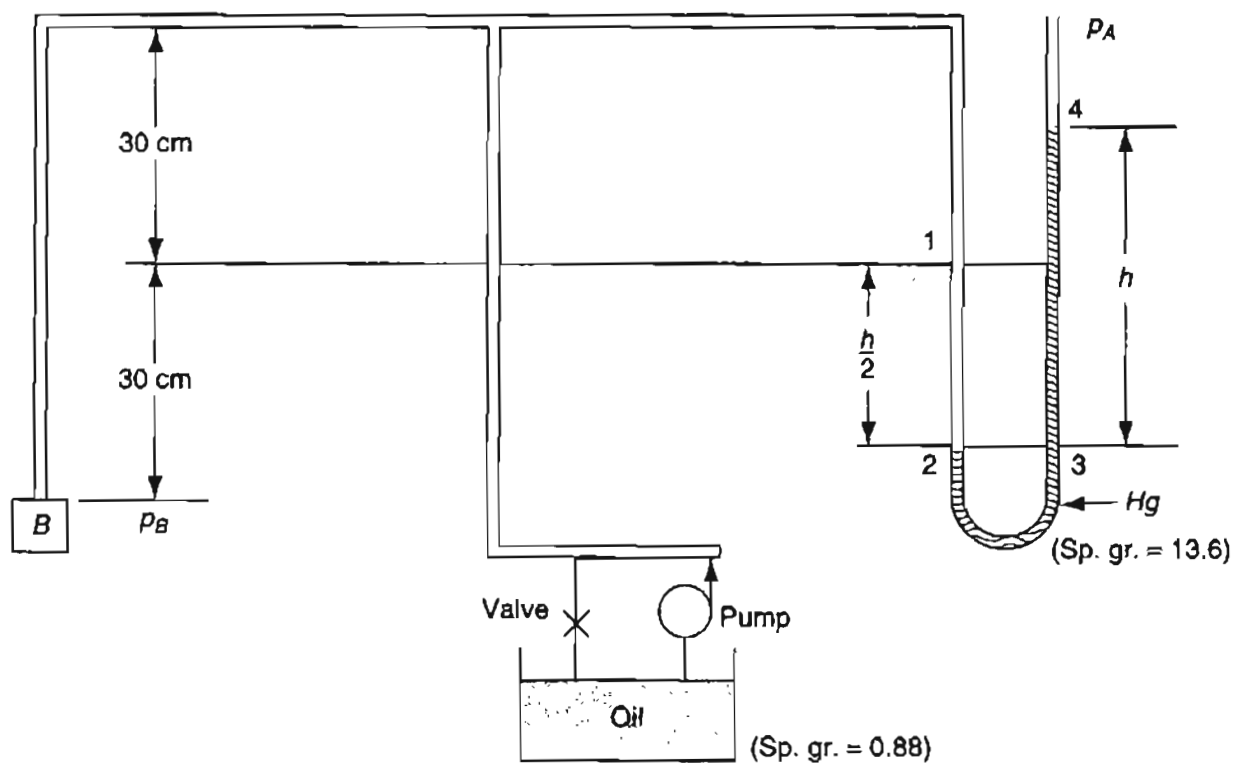


Figure P5.25

- 98**5.26 Examine Figure P5.26. Given that $a = 7.5$ in. and $b = 12$ in., what is the height of the water in the right hand vessel?

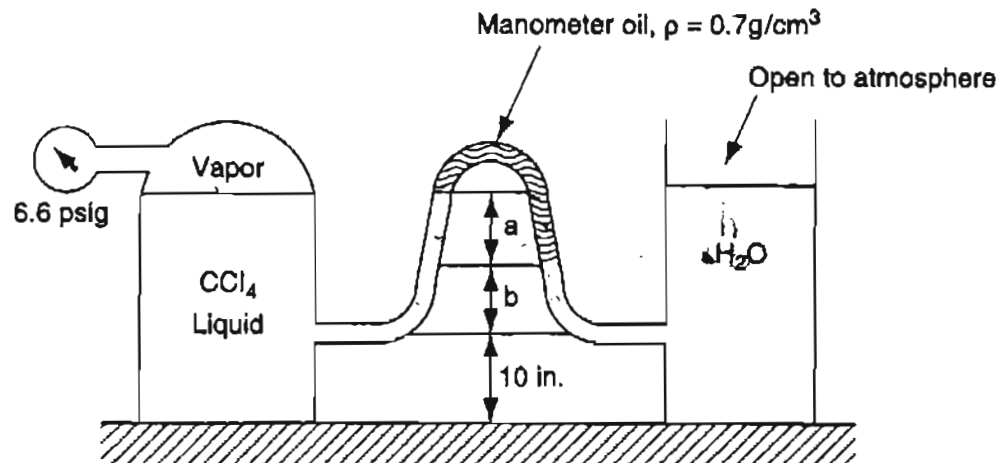


Figure P5.26

- 9*5.27 A differential pressure transmitter (DPT) can be used to sense the liquid level in a tank. See Figure P5.27.

How much error is made in not taking into account the height of the vapor above the liquid?

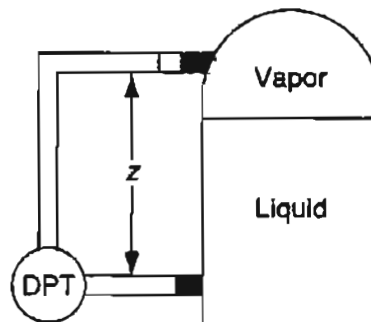


Figure P5.27

- *5.28 Deflagration is quick but progressive combustion (with or without explosion) as distinguished from a detonation which is the instantaneous decomposition of combustible material. (The National Fire Protection Association in Standard NFPA 68 has some more precise technical definitions.) For dust, the rate of deflagration depends on the particle size of the dust. NFPA gives a formula to calculate the area for venting a building to prevent structural damage on deflagration

$$A_v = CA_s/p^{0.5}$$

where A_v is the necessary vent area (ft^2 or m^2), C is a constant that must be determined by experiment (NFPA68 lists some values), A_s is the surface area of the build-

ing, and p is the maximum internal (gauge) pressure that can be sustained by the building without damage occurring.

In a proposed grain storage elevator 8m in diameter and 10m tall, the vented area (between the roof and top walls) is 10.4m^2 . Is this area sufficient if the elevator is designed to have a maximum overpressure of 7.5 kPa (7.5 kPa difference between the inside and outside)? Assume for grain dust that $C = 0.41(\text{kPa})^{0.5}$. Note the vents should be distributed in practice uniformly throughout the structure.

- *5.29 Pressure in a gas cell is measured with an inverted manometer, as shown in Figure P5.29. The scale on the far right-hand side of the figure shows the distances in mm (not to scale) of the interfaces of the liquids in the manometer. What is the pressure in the cell? $p_1 = 12.50$ psia.

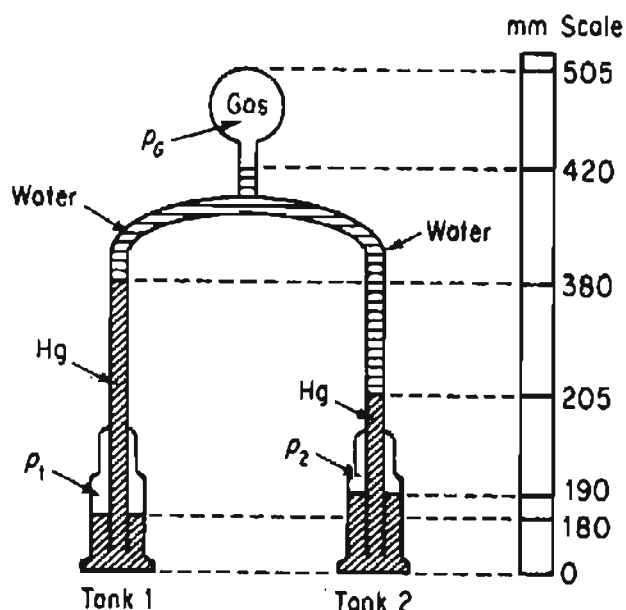


Figure P5.29

- *5.30 The indicating liquid in the manometer shown in Figure P5.30 is water, and the other liquid is benzene. These two liquids are essentially insoluble in each other. If the manometer reading is $\Delta Z = 36.3$ cm water, what is the pressure difference in kPa? The temperature is 25°C .

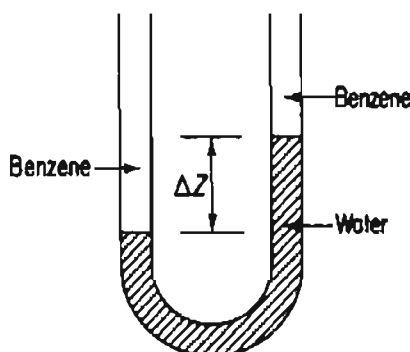


Figure P5.30

- **5.31** A U-tube differential mercury manometer is connected between two pipes. One pipe contains carbon tetrachloride (sp.gr. 1.59) under a pressure of 103 kPa, and the other pipe contains oil (sp.gr. 0.8) under a pressure of 172 kPa. Find the manometer reading h in meters.

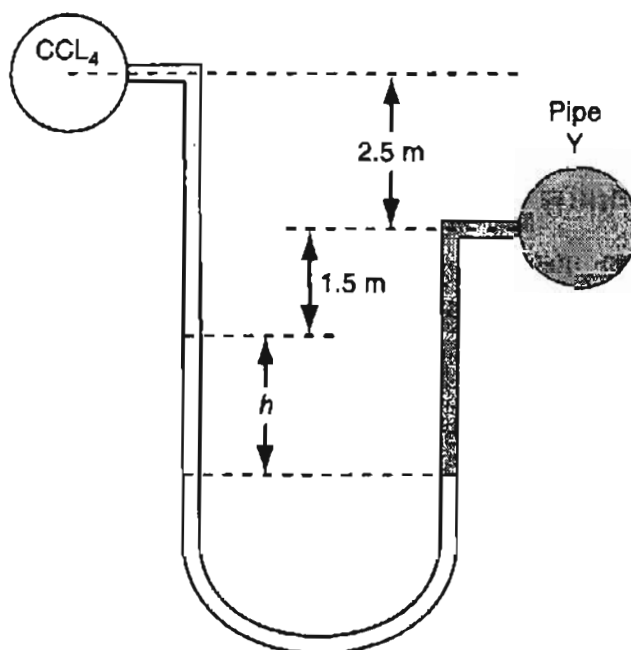


Figure P5.31

- **5.32** Examine the pressure measuring device shown in the figure. What is the gage pressure reading in psi at point A? The density of C_7H_{16} is 0.684 g/cm^3 .

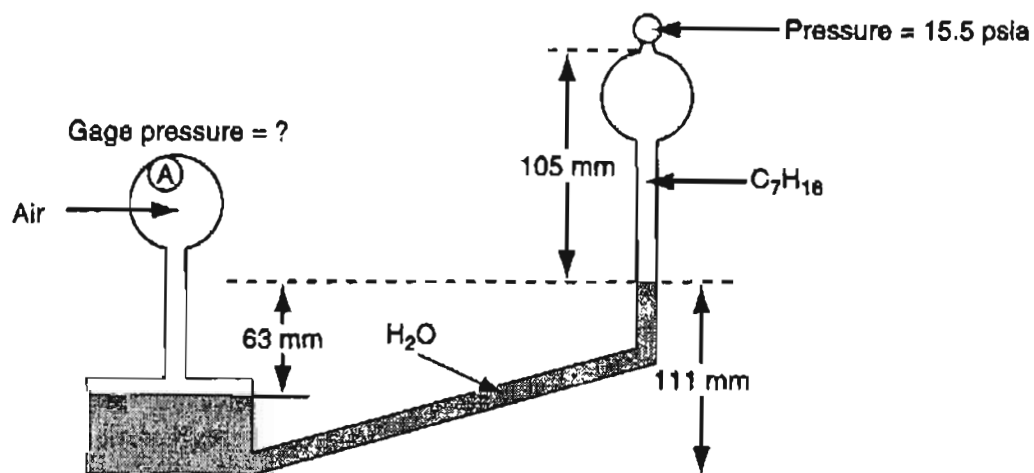


Figure P5.32

- *5.33** Examine Figure P5.33. Water flows through an orifice.

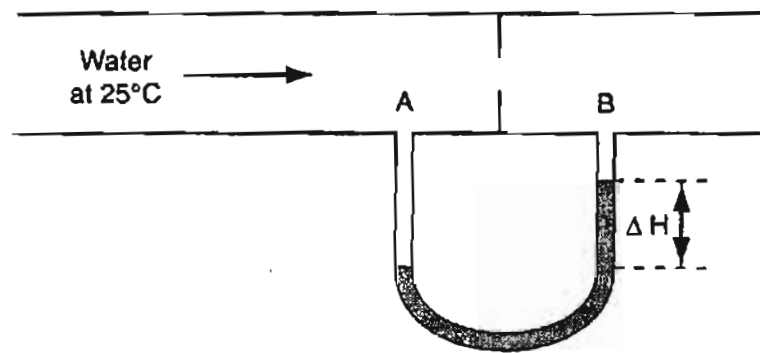


Figure P5.33

The manometer fluid has a specific gravity of 1.30. What is the pressure difference between points A and B in kPa if there is a 3.1 cm difference in the heights of the two columns of manometer fluid?

104 ✓***5.34 Examine Figure P5.34. The barometric pressure is 720 mm Hg. The density of the oil is 0.80 g/cm^3 . The Bourdon gauge reads 33.1 psig. What is the pressure in kPa of the gas?

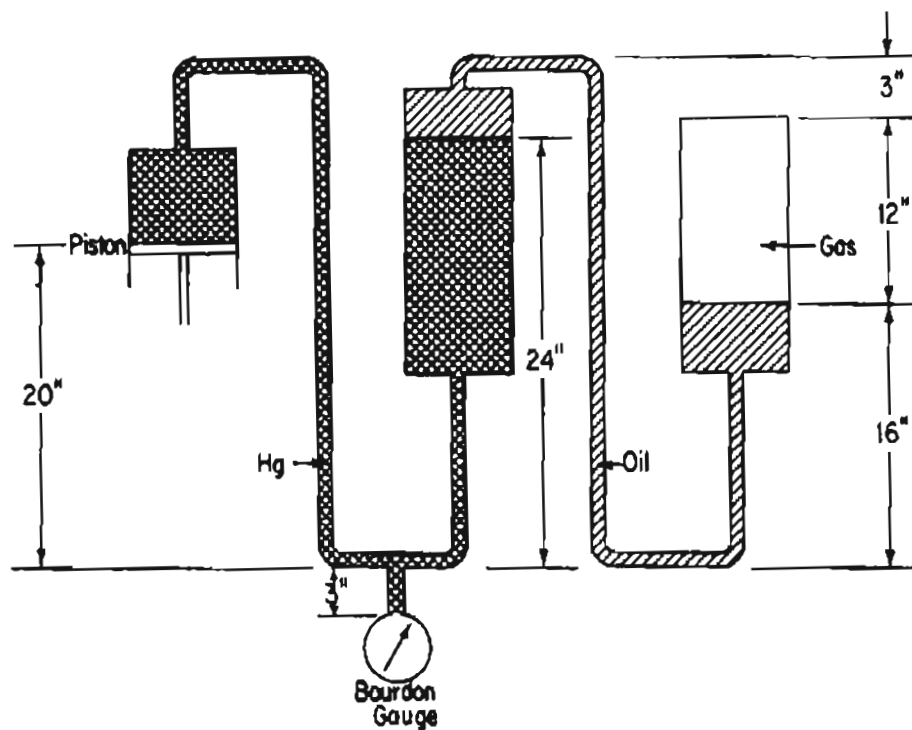


Figure P5.34

PART 2

MATERIAL BALANCES

CHAPTER	PAGE
6 Introduction to Material Balance	133
7 General Strategy for Solving Material Balance Problems	166
8 Solving Material Balance Problems for Single Units Without Reaction	196
9 The Chemical Equation and Stoichiometry	225
10 Material Balances for Processes Involving Reaction	260
11 Material Balance Problems Involving Multiple Units	305
12 Recycle, Bypass, and Purge and the Industrial Application of Material Balances	341

*If people knew how hard I worked to get my mastery,
it wouldn't seem so wonderful after all.*

Michelangelo

In Part 2 you begin to learn what material balances are all about. Material balances are nothing more than the application of the conservation law for mass: "Matter is neither created nor destroyed." Just what this statement means in practice, and how you can use the concept to solve problems of varying degrees of complexity, requires some fairly extensive explanation.

Look at Figure Part 2.1. Material balances were used to design the plant. You will also find that material balances are carried out in the plant during its operation for various time periods such as a year, a month, a day, and so on. The objective is to improve efficiency, maintain production, reduce environmental discharges, and maintain control of the processes in the plant. Material balances allow you to understand what is occurring in a processing plant. There is nothing mysterious or complicated about material balances. They are basically accounting—not for money, but for material.

"... the long years of education are mostly concerned with knowledge. Fact is piled upon fact and little if any time is spent in thinking. . . . On the whole it must be more important to be skilled in thinking than to be stuffed with facts."

E. de Bono, *The Five Day Course in Thinking* (1967)

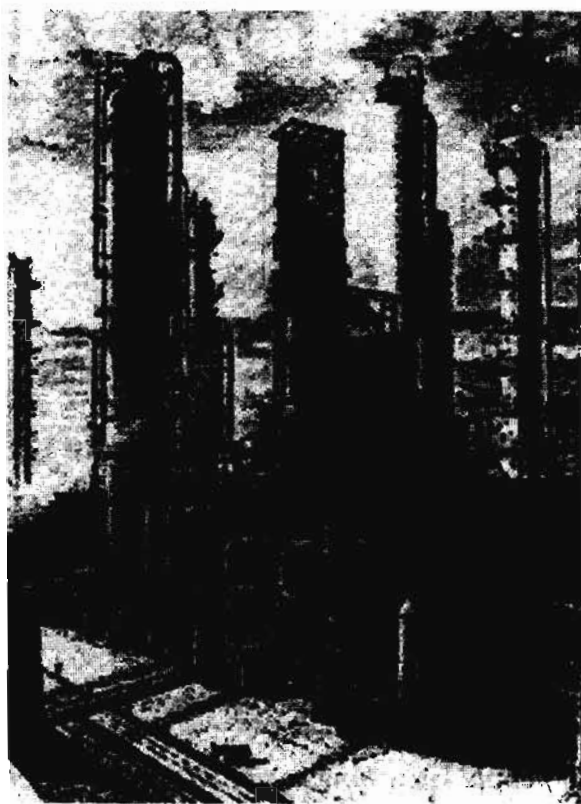


Figure Part 2.1. A section of a processing plant.

Why study material balances as a separate topic? You will find that material balance equations are almost invariably a prerequisite to all other calculations in the solution of both simple and complex chemical engineering problems. Furthermore, the skills that you develop in analyzing material balances are easily transferred to other types of balances and other types of problems.

In solving material balance problems, you must first develop an understanding of the problem. You must be able to visualize the problem from the problem statement, and to do so, you must be familiar with the terminology of the field. Once you understand the problem, you are ready to solve it. You will find that solving material balance problems is much easier if you develop a systematic strategy that is applicable to a wide range of problems. Consequently, in Chapter 7 we focus on the strategy of making appropriate decisions, implementing them properly, and assessing whether the implementation has been correct in solving a problem.

Our aim is to help you acquire a generalized approach to problem solving so that you may avoid looking upon each new problem, unit operation, or process as entirely new and unrelated to anything you have seen before. As you scrutinize the examples used to illustrate the principles involved in each chapter, explore the method of analysis, but avoid memorizing each example by rote, because, after all, they are only samples of the myriad of problems that exist or could be devised on the subject of material

balances. Although material balances are introduced in this part of the text, material balances are involved throughout the remainder of this text, and, for that matter, the remainder of your undergraduate program of study and thereafter.

GLOSSARY OF MISSING TERMS

Check (the answer) The step that demolishes your work.

Clearly Incomprehensible.

Difficult problem I don't know the answer (cf. Trivial).

Obvious I can't prove it.

Previous At some unknown time.

Similarly Too complicated to explain.

Trivial problem I know the answer.

SUPPLEMENTARY REFERENCES

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CHAPTER 6

INTRODUCTION TO MATERIAL BALANCES

6.1 The Concept of a Material Balance	134
6.2 Open and Closed Systems	136
6.3 Steady-State and Unsteady-State Systems	138
6.4 Multiple Component Systems	144
6.5 Accounting for Chemical Reactions in Material Balances	149
6.6 Material Balances for Batch and Semi-Batch Processes	151

Your objectives in studying this chapter are to be able to

1. Understand the features of open, closed, steady-state, and unsteady-state systems, and given a process in words or pictures, select the appropriate categories for the process.
2. Express in words what the material balance is for a process involving single or multiple components.
3. Determine whether positive or negative accumulation occurs in a process.
4. Understand the manner in which a chemical reaction affects the material balance.
5. Recognize a batch or semi-batch process and write the material balance for it.

Why spend time studying an introduction to material balances? Why not just start solving problems? You will find this chapter essential to all of the subsequent chapters because it explains the specialized terminology ("jargon") associated with making material balances. The chapter also eases you into the subject of material balances by using elementary examples so that you can proceed to more complex problems without stumbling.

Looking Ahead

This chapter introduces the concept of material balances, and demonstrates their application to different types of processes. We will use several simple systems to do so. Using these examples, we will construct a general material balance equation that you can apply to problems in the remainder of this text and in your professional career.

Most of the principles we consider in this chapter are of about the same degree of complexity as the law of compensation devised by some unknown, self-made philosopher who said: "Things are generally made even somewhere or some place. Rain always is followed by a dry spell, and dry weather follows rain. I have found it an invariable rule that when a man has one short leg, the other is always longer!"

6.1 The Concept of a Material Balance

Success is a journey, not a destination.

Jerry Baird

What are **material balances**? A material balance is nothing more than the application of the law of the **conservation of mass**: "Matter is neither created nor destroyed." Although the conservation of mass is a simple concept, detailed explanations are required to enable you to be able to apply it to a full range of chemical engineering systems.

You can get a good idea of what is involved in making a material balance by looking at a bank statement such as the one below, which illustrates the entries in a checking account.

BANK OF THE WEST CUSTOMER SUMMARY INFORMATION

Date	Notes	Deposit	Withdrawal	Balance
3/1	Beginning balance			\$1253.89
3/2	Deposit from ABC Co.	\$1500.00		\$2753.89
3/3	Check No. 2133		\$550.00	\$2203.89
3/3	ATM withdrawal 3/2		\$200.00	\$2003.89
3/5	Check No. 2134		\$401.67	\$1602.22
3/15	Check No. 2135		\$321.83	\$1280.39
3/18	ATM withdrawal 3/17		\$200.00	\$1080.39
3/20	Deposit at the bank	\$1250.00		\$2330.39
3/23	Check No. 2136		\$442.67	\$1887.72
3/31	Service charge		\$10.00	\$1877.72
3/31	Closing balance			\$1877.72

The checking account initially has a balance of \$1253.89, which is the **initial condition** of the account. Deposits (**what goes in, the inputs**) are added to the account, and withdrawals (**what goes out, the outputs**) are subtracted from the account. The **final condition** of the account is the closing balance (\$1877.72). Can you write an equation that expresses the closing balance in terms of the beginning balance and the deposits and withdrawals? Would you agree that the following relation in words represents the information presented in the checking account:

$$\begin{aligned}\text{Closing balance} - \text{Beginning balance} &= \text{Sum of the deposits} \\ &\quad - \text{Sum of the withdrawals}\end{aligned}$$

or

$$\text{Final condition} - \text{Initial condition} = \text{Sum of inputs} - \text{Sum of outputs}$$

You can check these equations by substituting the values from the bank statement for the words. In this case, the checking account increased by \$633.83, namely \$1877.72 - \$1253.89, indicating an **accumulation** of money in the account. The accumulation is equal to the final condition minus the initial condition.

Chemical processes are similar in many ways to the checking account. Material balances pertain to materials rather than money as you can infer from the name, but the concepts of balancing money and materials are exactly the same. The initial conditions for a process involve the amount of material initially present in the process. Deposits into the checking account are analogous to the flow of material into a process and withdrawals are analogous to the flow of material out of a process. Accumulation of material in a process results when the flow of material into the process is greater than the flow out.

Here is another example of making money balances in the form of a puzzle. Three students rent a room the night before the game, and pay the desk clerk \$60. A new clerk comes on duty, and finds that the discounted rate for students should have been \$55. The new clerk gives the bellhop \$5 to return to the students, but the bellhop, not having change and being slightly dishonest, returns only \$1 to each student, and keeps the remaining \$2. Now each student paid \$20 - \$1 = \$19, and $3 \times \$19 = \57 paid in total. The bellhop kept \$2 for a total of \$59. What happened to the other \$1?

Apply what you have learned so far to solve the puzzle. It provides a good, simple illustration of the confusion that can be cleared up by making a material (here, dollar) balance. (If the puzzle stumps you, look at the end of this chapter for the answer.)

SELF-ASSESSMENT TEST

Questions

1. What is the difference between the law of the conservation of mass and the concept of the material balance?
2. Define material balance.

Problem

1. Draw a sketch of the following processes, and place a dashed line appropriately to designate the system:
 - a. a tea kettle
 - b. a fireplace
 - c. a swimming pool.

Thought Problems

1. Name some quantities besides mass that are conserved.
2. Mr. Ledger deposited \$1000 in his bank account, and withdrew various amounts of money as listed in the following schedule:

Withdrawals	Amount left
\$500	\$500
250	250
100	150
80	70
50	20
20	0
Total \$1000	\$990

The withdrawals total \$1000, but it looks as if Mr. Ledger had only \$990 in the bank. Does he owe the bank \$10?

6.2 Open and Closed Systems

In this section we will explain what the terms open and closed systems mean, concepts that are quite important, and will be used extensively in the remainder of this book.

What's in a name? That which we call a rose by any other name would smell as sweet.

Wm. Shakespeare in *Romeo and Juliet*

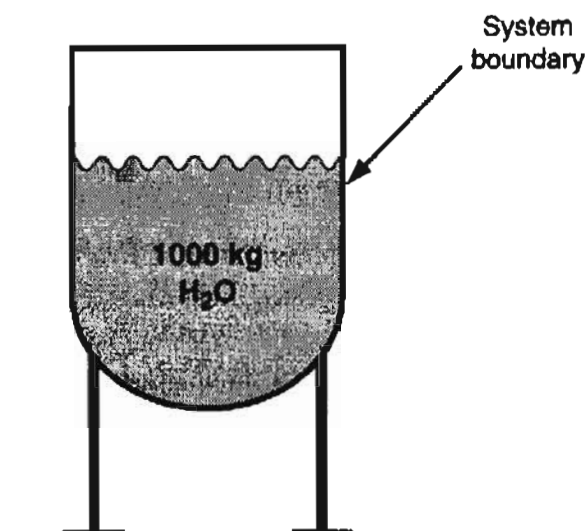


Figure 6.1 A closed system.

a. System.

By **system** we mean any arbitrary portion of or a whole process that you want to consider for analysis. You can define a system such as a reactor, a section of a pipe, or an entire refinery by stating in words what the system is. Or, you can define the limits of the system by drawing the **system boundary**, namely a line that encloses the portion of the process that you want to analyze. The boundary could coincide with the outside of a piece of equipment or some section inside the equipment. Now, let us look at two important classes of systems.

b. Closed system.

Figure 6.1 shows a two-dimensional view of a three-dimensional vessel holding 1000 kg of H₂O. Note that material neither enters nor leaves the vessel, that is, no material crosses the system boundary. Figure 6.1 represents a **closed system**. Changes can take place inside the system, but for a closed system, no mass exchange occurs with the surroundings.

c. Open system.

Next, suppose that you add water to the tank shown in Figure 6.1 at the rate of 100 kg/min and withdraw water at the rate of 100 kg/min, as indicated in Figure 6.2. Figure 6.2 is an example of an **open system** (also called a **flow system**) because material crosses the system boundary.

SELF-ASSESSMENT TEST

Questions

1. Is it true that if no material crosses the boundary of a system, the system is a closed system?
2. In an automobile engine, as the valve opens to a cylinder, the piston moves down and air enters the cylinder. Fuel follows, and is burned. Thereafter, the combustion gases are dis-

charged as the piston moves up. On a very short time scale, say a few microseconds, would the cylinder be considered an open or closed system? Repeat for a time scale of several seconds.

Problems

1. Label the materials entering and leaving the systems listed in Problem 1 in Section 6.1. Designate the time interval of reference as short or long, and classify each system as open or closed.
2. Classify the following processes as (a) open, (b) closed, (c) neither, or (d) both for a characteristic operating interval:
 - a. Oil storage tank at a refinery
 - b. Flush tank on a toilet
 - c. Catalytic converter on an automobile
 - d. Gas furnace in a home
3. As an example of a system, consider a water heater.
 - a. What is *in* the system?
 - b. What is *outside* the system?
 - c. Is the system open or closed?

6.3 Steady-State and Unsteady-State Systems

In this section we will describe the characteristics of steady-state and unsteady-state systems. The former represents the majority of the processes you will encounter in industry, and in the examples and problems in this book.

a. Steady-state system.

Because the rate of addition of water is equal to the rate of removal, the amount of water in the vessel shown in Figure 6.2 remains constant at its origi-

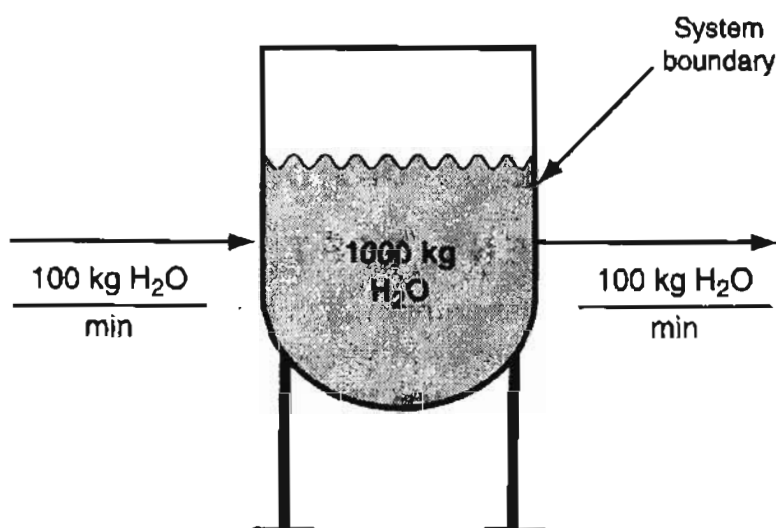


Figure 6.2 An open steady-state system.

nal value (1000 kg). We call such a process or system a **steady-state process** or a **steady-state system** because

- 1) the conditions inside the process (specifically the amount of water in the vessel in Figure 6.2) remain unchanged with time, and
- 2) the conditions of the flowing streams remain constant with time.

Thus, in a steady-state process, by definition all of the conditions in the process (e.g., temperature, pressure, mass of material, flow rate, etc.) remain constant with time. A **continuous process** is one in which material enters and/or leaves the system without interruption.

b. Unsteady-state system.

What if you make a change in the process so that the flow out of the system is instantaneously reduced to a constant 90 kg/min? Figure 6.3 shows the initial condition in the vessel. Because water accumulates at the rate of 10 kg/min (100 kg/min—90 kg/min) in the system, the amount of water present in the vessel will depend on the interval of time for which the rate of accumulation is maintained. Figure 6.4 shows the system after 50 minutes of accumulation. (Fifty minutes of accumulation at 10 kg/min amounts to 500 kg of total accumulation.) Because the amount of water in the system changes with time, the process and system are deemed to be an **unsteady-state (transient) process or system**. For an unsteady-state process, not all of the conditions in the process (e.g., temperature, pressure, mass of material, etc.) remain constant with time, and/or the flows in and out of the system can vary with time.

What else might you change about the process we have been analyzing? Suppose you make the flow out of the system 100 kg/min again, and reduce the flow into the system to 90 kg/min. Figure 6.5 shows the initial conditions for this system. Note that the amount of water in the system decreases with time at the rate of 10 kg/min. Figure 6.6 shows the system after 50 minutes of operation. Figures 6.5

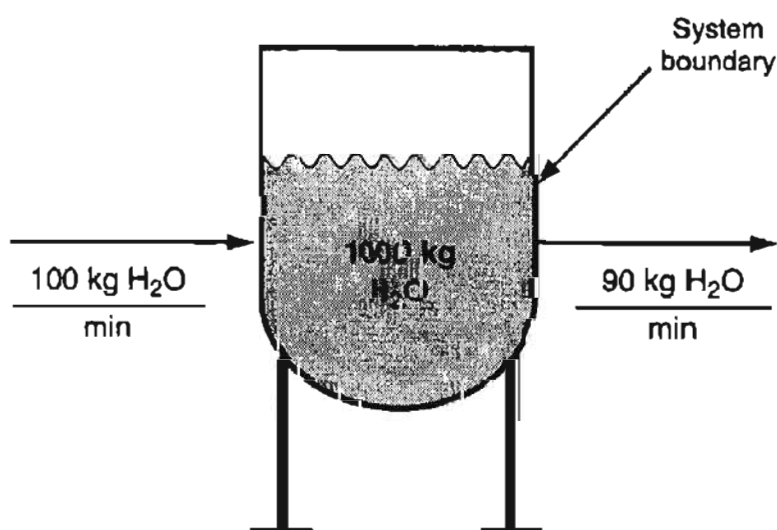


Figure 6.3 Initial conditions for an open unsteady-state system with accumulation.

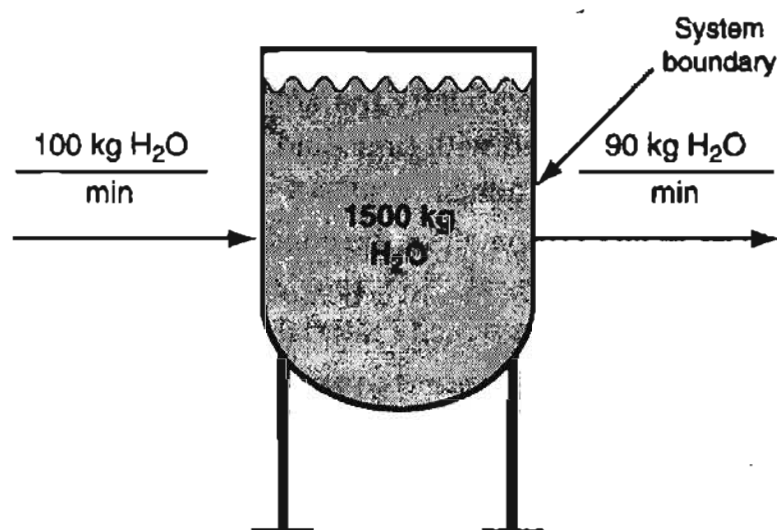


Figure 6.4 The condition of the open unsteady-state system with accumulation after 50 minutes.

and 6.6 demonstrate **negative accumulation**, another illustration of an unsteady-state process.

From these examples of different systems, let us generalize to obtain a simple but very important equation: In words, the material balance for a single component process is

$$\left\{ \begin{array}{c} \text{Accumulation of material} \\ \text{within the system} \end{array} \right\} = \left\{ \begin{array}{c} \text{Total flow into} \\ \text{the system} \end{array} \right\} - \left\{ \begin{array}{c} \text{Total flow out} \\ \text{of the system} \end{array} \right\} \quad (6.1)$$

Figures 6.2 through 6.6 show the mass flows and initial and final conditions. However, Equation (6.1) does not specifically refer to mass but to "material" and "flows." Equation (6.1) can apply to moles or any quantity that is conserved. As an example, look at Figure 6.7 in which we have converted all of the mass quantities in Figure 6.2 to their equivalent values in moles.

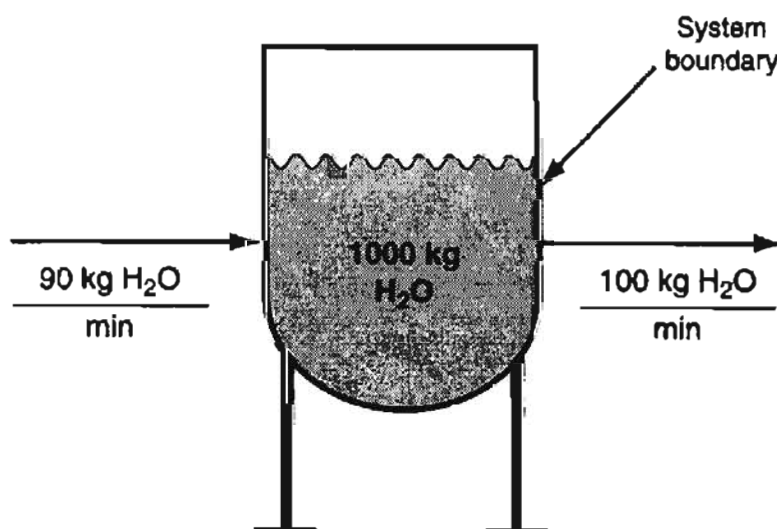


Figure 6.5 Initial conditions for an unsteady-state process with negative accumulation.

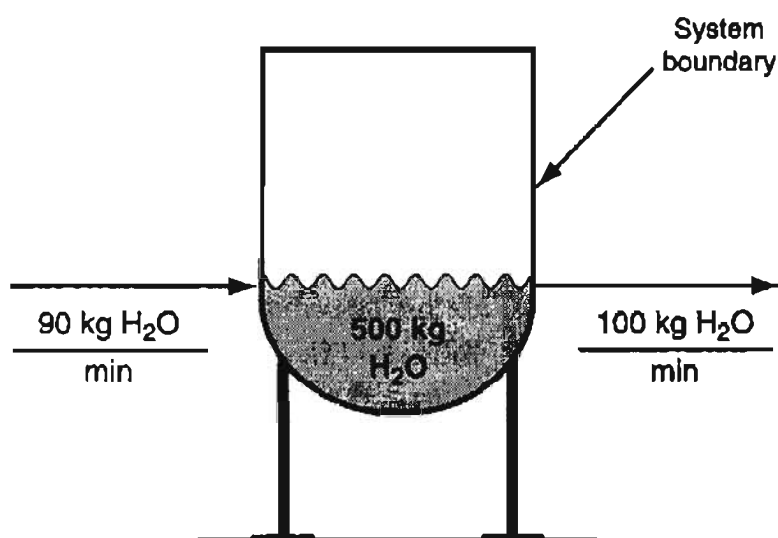


Figure 6.6 Condition of the open unsteady-state system with negative accumulation after 50 minutes.

When you apply Equation (6.1) to a material balance problem, if the process is in the steady state, the accumulation term by definition is zero, and Equation (6.1) simplifies to a famous truism

$$\text{What goes in must come out} \quad (6.2)$$

If you are analyzing an unsteady-state process, the accumulation term over a time interval can be calculated as

$$\{\text{Accumulation}\} = \left\{ \begin{array}{l} \text{Final material} \\ \text{in the system} \end{array} \right\} - \left\{ \begin{array}{l} \text{Initial material} \\ \text{in the system} \end{array} \right\} \quad (6.3)$$

The times you select for the final and initial conditions can be anything, but you usually select an *interval* such as 1 minute or 1 hour rather than specific times. When you combine Equations (6.1) and (6.3) you get the general material balance for a component in the system *in the absence of reaction*

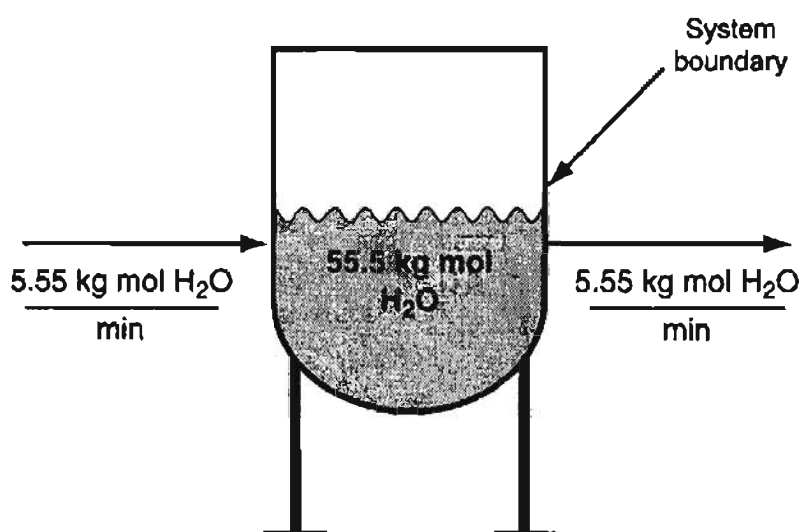


Figure 6.7 The system in Figure 6.2 with the flow rates shown in kg mol.

$$\left\{ \begin{array}{c} \text{Final material} \\ \text{in the system} \\ \text{at } t_2 \end{array} \right\} - \left\{ \begin{array}{c} \text{Initial material} \\ \text{in the system} \\ \text{at } t_1 \end{array} \right\} = \left\{ \begin{array}{c} \text{Flow into} \\ \text{the system} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} - \left\{ \begin{array}{c} \text{Flow out of} \\ \text{the system} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} \quad (6.4)$$

If you pick a basis of 1 hour, for example, to solve a problem, the accumulation term represents the sum (or integral) of all of the material that has accumulated in the system during the time interval. The units of the accumulation are mass or moles, not mass or moles per unit time. Similarly, the flows in and out represent the sum (or integral) of all of the flows of mass or moles in and out, respectively, during the time interval, and not the flows per unit time, which would be called *rates*. If rates are given in the problem, you multiply by your selected time interval (such as 1 hour) to get all of the entering or exit mass or moles. Consequently, Equation (6.4) can be deemed to be the result of integrating a material balance if the balance were formulated as a *differential equation*. Refer to Chapter 32 for a detailed discussion of material balances represented as differential equations.

EXAMPLE 6.1 A Material Balance for the Blending of Gasoline

Will you save money if instead of buying premium 89 octane gasoline at \$1.269 per gallon that has the octane you want, you blend sufficient 93 octane supreme gasoline at \$1.349 per gallon with 87 octane regular gasoline at \$1.149 per gallon?

Solution

This problem is an example of applying Equation (6.4) to neither mass nor moles but to octane number (ON). ON is the ratio of the number of engine knocks per unit time using the gasoline being tested to the number of engine knocks per unit time using iso-octane in a standardized engine. ON is approximately linearly related to the ON-enhancer concentration in the gasoline. This linear relationship is the basis of a principle that states that the product of the ON of the solution times the volume of the solution is a quantity that is conserved.

Choose a basis of 1 gallon of 89 octane gasoline, the desired product. Examine Figure E6.1. The system is the gasoline tank.

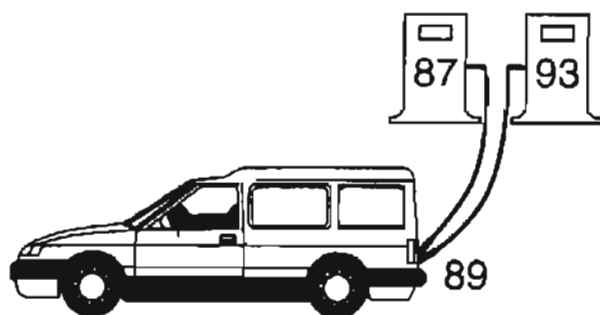


Figure E 6.1

First you have to decide whether the system is open or closed, and whether it is steady-state or unsteady-state. For simplicity, assume that no gasoline exists in the tank at the start of the blending, and one gallon exists in the tank at the end of the blending. This arrangement corresponds to an unsteady-state process. Clearly it is an open system. The flows into the system are the number of (fractional) gallons of each of the two grades of gasoline.

The initial number of gallons in the system is zero and the final number of gallons is one. Suppose we let x be the number of gallons of 87 octane gasoline added, and y be the number of gallons of 93 octane added to the blend. Since $x + y = 1$ is the total flow into the tank, you know that $y = 1 - x$. According to Equation (6.4) the balance on the ON is

$$\begin{array}{c} \text{Accumulation} \\ \left| \frac{89 \text{ octane}}{1 \text{ gal}} \right| \frac{1 \text{ gal}}{1} - 0 = \begin{array}{c} \text{Inputs} \\ \left| \frac{87 \text{ octane}}{1 \text{ gal}} \right| \frac{x \text{ gal}}{1} + \left| \frac{93 \text{ octane}}{1 \text{ gal}} \right| \frac{(1 - x) \text{ gal}}{1} \end{array} \end{array}$$

The solution is $x = 2/3$ gal and thus $y = 1/3$ gal.

The cost of the blended gasoline is

$$2/3 (\$1.149) + 1/3 (\$1.349) = \$1.216$$

a value less than the cost of the 89 octane gasoline (\$1.269). In practice, refineries usually take into account the nonlinear blending of gasoline (unlike the linear blending considered here) with different octane numbers because one or two tenths of an octane number amounts to a significant amount of money because of the volume of gasoline that they sell.

SELF-ASSESSMENT TEST

Questions

1. Is mass conserved within an open process?
2. Without looking at the text write down the equation that represents a material balance in (a) an open system and (b) a closed system.
3. Can an accumulation be negative? What does a negative accumulation mean?
4. Under what circumstances can the accumulation term in the material balance be zero for a process?
5. Distinguish between a steady-state and an unsteady-state process.
6. What is a transient process? Is it different than an unsteady-state process?

Problem

1. Classify the systems in the Self-Assessment Test Problem #2 of Section 6.2 as (a) steady-state, (b) unsteady-state, (c) neither, or (d) both.

Thought Problems

1. Examine Figure TP6.3P1.

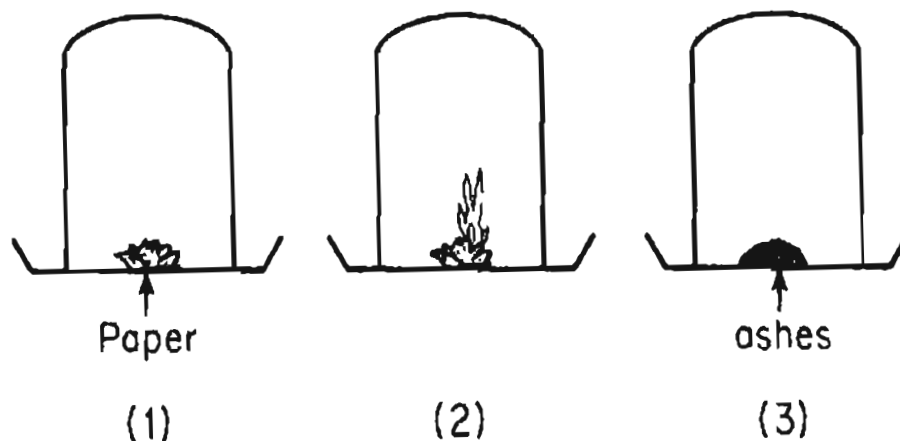


Figure TP6.3P1

A piece of paper is put into the bell in (1). In picture (2) you set fire to the paper. Ashes are left in picture (3).

If everything is weighed (the bell, the dish, and the materials) in each of the three cases, you would find:

- a. Case 1 would have the larger weight.
 - b. Case 2 would have the larger weight.
 - c. Case 3 would have the larger weight.
 - d. None of the above.
2. Certain critical processes require a minimum fluid flow for safe operation during the emergency shutdown of a plant. For example, during normal operation in one process, the chlorine is removed safely from the processing unit along with the flowing liquids. But during an emergency shutdown, the chlorine collects in the unit and its pipeline headers. Hence a minimum flow rate is needed to remove the chlorine. If the unit and pipelines are considered to be one system, how can a minimum flow rate be obtained for safe operation if the electric power and controller fail?

Discussion Problem

1. Why is the transient analysis of a process important in the overall analysis of a process?

6.4 Multiple Component Systems

Now, let us examine a slightly more complicated process. All the Figures so far have illustrated the flow of water—a single component. Suppose the input to a vessel contains more than one component, such as 100 kg/min of a 50% water and

50% sugar (sucrose, $C_{12}H_{22}O_{11}$, MW 342.3) mixture. As indicated in Figure 6.8, the vessel initially contains 1000 kg of water, and the exit stream flow is 100 kg/min of water and sugar. How would the material balance for the process in Figure 6.8 differ from the ones displayed in Figures 6.1 through 6.6?

After examining Figure 6.8, would you agree that because the constant total inlet mass flow of 100 kg/min equals the constant total exit mass flow of 100 kg/min, the system can be represented as a steady-state system insofar as a balance on the total mass is concerned? However, with respect to the sugar and water mass balances, balances that we call **component balances**, the process will be unsteady-state. Sugar starts to accumulate in the system and water is depleted.

Now look at the mixer shown in Figure 6.9, an apparatus that mixes two streams to increase the concentration of NaOH in a dilute solution. The mixer is a steady-state open system. Initially the mixer is empty, and after 1 hour it is empty again. We will use the values of the components listed in Figure 6.9 to show you how the total and component balances for mass and moles are made according to Equations (6.4) and (6.1). Because we deemed the process to be in the steady state, we do not have to be concerned about the initial and final conditions *in* the tank—they remain unchanged. Furthermore, if the tank is well mixed, the concentration of a component in the output stream will be the same as the concentration of the component inside the tank during the hour of mixing.

Because the flows in Figure 6.9 are expressed in kg/hr, we will choose a basis of 1 hour for convenience so that the time variable does not have to be carried along in each mass balance. We multiplied each rate by 1 hour to get the values for the kg listed for each stream in Figure 6.9. As an alternate to the basis we selected you could select $F_1 = 9000$ kg/hr as the basis, or $F_2 = 1000$ kg/hr as the basis; the num-

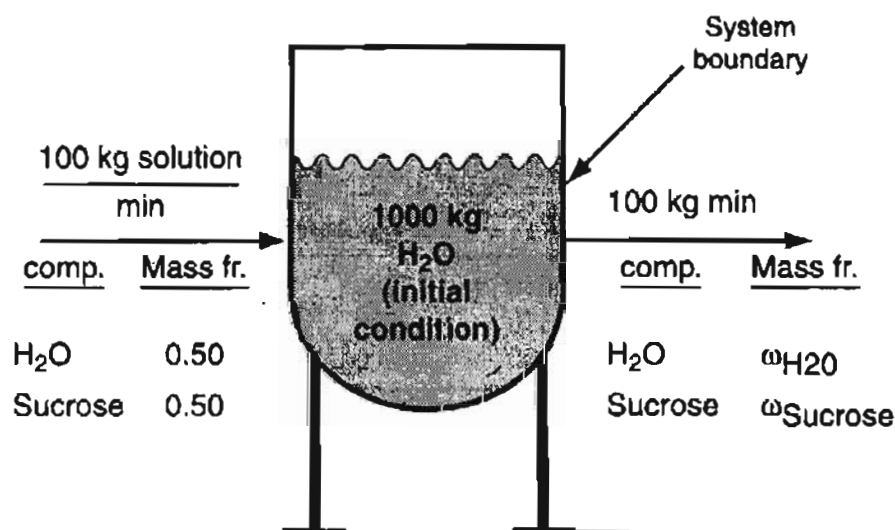


Figure 6.8 An open system involving two components.

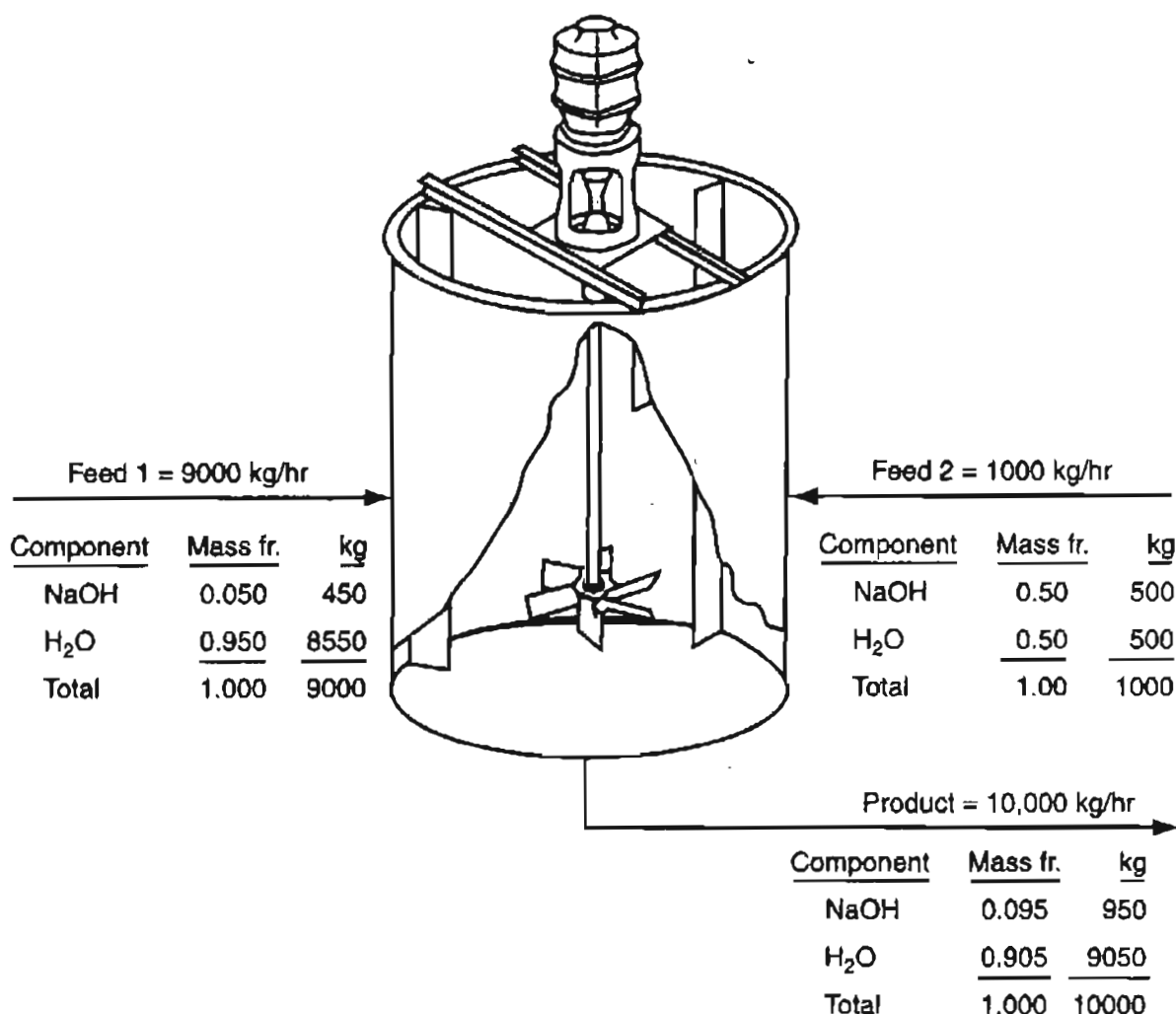


Figure 6.9 Mixing of a dilute stream of NaOH with a concentrated stream of NaOH. Values below the stream arrows are based on 1 hour of operation.

bers for this example would not change—just the units would change. Here are the component and total balances in kg:

Balances	Flow in		Flow out	Accum.
	F_1	F_2		
NaOH	450	500	950	= 0
H ₂ O	8,550	500	9,050	= 0
Total	9,000	1,000	10,000	= 0

Next, we will show the application of Equation (6.4) in terms of moles for the process in Figure 6.9. We can convert the kg shown in Figure 6.9 to kg moles by dividing each compound by its respective molecular weight (NaOH = 40 and H₂O = 18).

$$\begin{array}{lll} \text{NaOH:} & \frac{450}{40} = 11.25 & \frac{500}{40} = 12.50 & \frac{950}{40} = 23.75 \\ \text{H}_2\text{O:} & \frac{8550}{18} = 475 & \frac{500}{18} = 27.78 & \frac{9050}{18} = 502.78 \end{array}$$

Then the component and total balances in kg mol are:

Balances	Flow in		Flow out	Accum.
	F_1	F_2		
NaOH	11.25	12.50	23.75	= 0
H ₂ O	475	27.78	502.78	= 0
Total	486.25	40.28	536.53	= 0

EXAMPLE 6.2 Concentration of Cells Using a Centrifuge

Centrifuges are used to separate particles in the range of 0.1 to 100 μm in diameter from a liquid using centrifugal force. Yeast cells are recovered from a broth (a liquid mixture containing cells) using a tubular centrifuge (a cylindrical system rotating about a cylindrical axis). Determine the amount of the cell-free discharge per hour if 1000 L/hr is fed to the centrifuge, the feed contains 500 mg cells/L, and the product stream contains 50 wt.% cells. Assume that the feed has a density of 1 g/cm³.

Solution

This problem involves a steady state, open (flow) system without reaction. Two components are involved: cells and broth. Take a convenient basis of 1 hour.

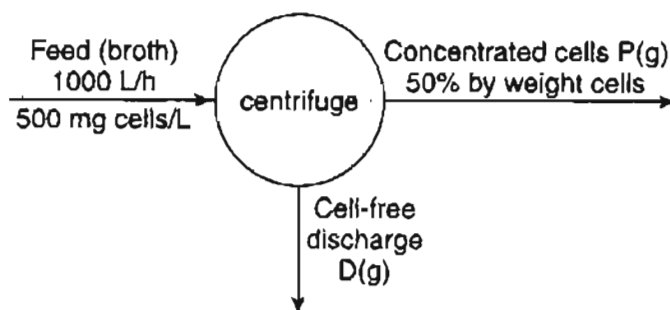


Figure E6.2

The material balance for the cells is the mass of cells that flow in must equal the mass of cells that flow out:

$$\frac{1000 \text{ L feed}}{1 \text{ L feed}} \left| \frac{500 \text{ mg cells}}{1000 \text{ mg}} \right| = \frac{0.5 \text{ g cells}}{1 \text{ g } P} \left| \frac{P \text{ g}}{1000 \text{ mg}} \right|$$

$$P = 1000 \text{ g}$$

The mass balance for the fluid is the mass of fluid that flows in equals the mass of fluid that flows out:

$$\frac{1000 \text{ L}}{1 \text{ L}} \left| \frac{1000 \text{ cm}^3}{1 \text{ cm}^3} \right| \left| \frac{1 \text{ g fluid}}{1 \text{ g } P} \right| = \frac{1000 \text{ g } P}{1 \text{ g } P} \left| \frac{0.50 \text{ g fluid}}{1 \text{ g } P} \right| + D \text{ g fluid}$$

$$D = (10^6 - 500) \text{ g}$$

$$10^6 - 1000$$

SELF-ASSESSMENT TEST

Questions

1. Does Equation (6.4) apply to a system involving more than one component?
2. When a chemical plant or refinery uses various feeds and produces various products, does Equation (6.4) apply to each component in the plant?

Problems

1. Here is a report from a catalytic polymerization unit:

Pounds per hour

Charge:

Propanes and butanes 15,500

Production:

Propane and lighter 5,680

Butane 2,080

Polymer missing

What is the production in pounds per hour of the polymer?

2. A plant discharges 4,000 gal/min of treated wastewater that contains 0.25 mg/L of PCBs (polychlorinated biphenyls) into a river that contains no measurable PCBs upstream of the discharge. If the river flow rate is 1,500 cubic feet per second, after the discharged water has thoroughly mixed with the river water, what is the concentration of PCBs in the river in mg/L?

Thought Problem

1. This true story was told to DMH by Professor Gene Woolsey:

Once upon a time a big manufacturer of canned frozen orange juice concentrate found that 12 to 15% of the concentrate disappeared some place between Florida and the storage warehouse in the Northeast. A chemical engineer was called on to solve the problem. When she arrived at the Florida plant, the first thing she noticed was a stink caused by a number of dead alligators floating on the surface of an adjacent lake. Ignoring the smell, she carefully

followed the processing of the orange juice from squeezing, through concentration, and cooling to slush. She watched the waiting trucks being steam cleaned and sanitized, and then the slush being pumped into the trucks prior to being sent off to the warehouse.

The trucks were weighed before and after filling. She placed a seal on one or two trucks, and flew to the warehouse district to wait for "her" trucks to come in. On arrival she noted that the seals were undisturbed. A pump was attached to the bottom drain of a truck, and the slush pumped out into a holding tank until the pump started sucking air, at which time the pump was disconnected.

Then she watched the cans being filled from the holding tank, counted the cans, had some weighed, and noted a minor amount of spillage, but the spillage and filling operation amounted to less than 1% of the overall loss. At this point she concluded that either (a) cheating was going on in Florida, and/or (b) someone was stealing cases of concentrate from the warehouse. She spent a couple of nights in the warehouse and did note someone take a couple of cases of concentrate, but that amount had negligible effect on the overall loss.

Two weeks later while drinking orange juice at breakfast, she had sudden idea as to what the company's problem was. What was it?

Discussion Problems

1. Isotope markers in compounds are used to identify the source of environmental pollutants, investigate leaks in underground tanks and pipelines, and trace the theft of oil and other liquid products. Both radioactive and isotopic markers are used.

Deuterium is typically used as a marker for organic compounds. Three or more hydrogen atoms on the organic molecule are replaced by deuterium. However, isotopes of carbon and oxygen can also be used. The detection limit of tracers using a combination of gas chromatography and mass spectrometry is about 100 ppb in crude oil and about 20 ppb in refined products.

Explain how such markers can be used in chemical processes.

2. Projects suggested to avoid climatic changes engendered by man's activities and in particular the increase in CO_2 in the atmosphere include dispersal of sulfate particles in the stratosphere to reflect sunlight and fertilizing the southern oceans with iron to stimulate phytoplankton growth. It is believed that low levels of iron limit the biological productivity of nutrient-rich southern oceans. Adding iron to these waters would increase the growth of phytoplankton, thus reducing CO_2 levels in the seawater and thereby altering the CO_2 balance between sea water and the atmosphere. What do you think of such a suggestion?

6.5 Accounting for Chemical Reactions in Material Balances

Chemical reaction in a system requires the augmentation of Equation (6.4) to take into account the effects of the reaction(s). To illustrate this point, look at Figure 6.10, which shows a steady-state system in which HCl reacts with NaOH by the following reaction: $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$.

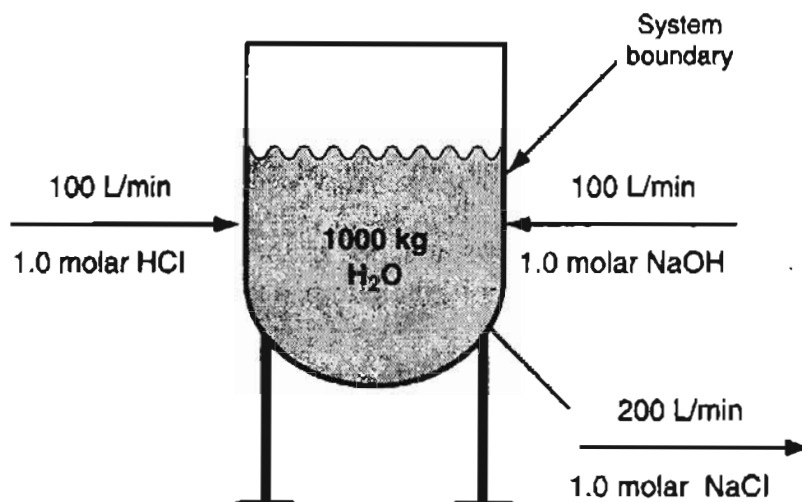


Figure 6.10 Reactor for neutralizing HCl with NaOH. The exit flow of 200 L/min is a rounded value.

Because 100 mol/min of HCl react with the stoichiometric amount of NaOH (100 mol/min), complete reaction is assumed to occur. Therefore, neither HCl nor NaOH is present in the product stream leaving the reactor. How should you account for the gain and loss of components in the system? Equation (6.4) must be augmented to include terms for the **generation** and **consumption** of components by the chemical reaction in the system as follows

$$\left\{ \begin{array}{c} \text{Accumulation} \\ \text{within the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{c} \text{Input} \\ \text{through} \\ \text{the system} \\ \text{boundaries} \end{array} \right\} - \left\{ \begin{array}{c} \text{Output} \\ \text{through} \\ \text{the system} \\ \text{boundaries} \end{array} \right\} + \left\{ \begin{array}{c} \text{Generation} \\ \text{within the} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{c} \text{Consumption} \\ \text{within the} \\ \text{system} \end{array} \right\} \quad (6.5)$$

We will defer to Chapter 10 the analysis of material balances for reacting systems. Even though reactors (i.e., vessels that promote chemical reactions) are the heart of most chemical plants, they comprise only a small portion of the total number of process units in most chemical plants. Therefore, a large majority of the process units in the chemical processing industries do not involve chemical reactions and Equation (6.4) can be used. The remainder of this chapter as well as Chapters 7 and 8 will focus on material balances for processes without chemical reaction.

SELF-ASSESSMENT TEST

Questions

- Write down the general material balance in words for a process in which reaction occurs.
- What terms of the general material balance, Equation (6.5), can be deleted if
 - the process is known to be a steady-state process.
 - the process is carried out inside a closed vessel.
 - the process does not involve a chemical reaction.

6.6 Material Balances for Batch and Semi-Batch Processes

A **batch process** is used to process a fixed amount of material each time it is operated. Initially, the material to be processed is charged into the system. After processing of the material is complete, the products are removed. Therefore, if you include the material originally charged into the vessel as well as the material remaining in the vessel after the processing has been completed as part of the system, batch processes fall into the category of closed systems. Batch processes are used industrially for speciality processing applications (e.g., producing pharmaceutical products), which typically operate at relatively low production rates. Look at Figure 6.11a that illustrates what occurs at the start of a batch process.

Two separate quantities of material are put into a mixing vessel at the start of the process, 9000 lb of H_2O and 1000 lb of NaOH (Figure 6.11a), and after thorough mixing, the final solution remains in the system (Figure 6.11b).

From the viewpoint of Equation (6.4), the flows by definition are zero because material does not cross the system boundary. Would you conclude that the accumulation of the total mass in the system is zero? Yes. All that happens in the batch system (in the absence of chemical reaction) insofar as the total mass or moles of material, or the mass or moles of the individual components, is that the final conditions

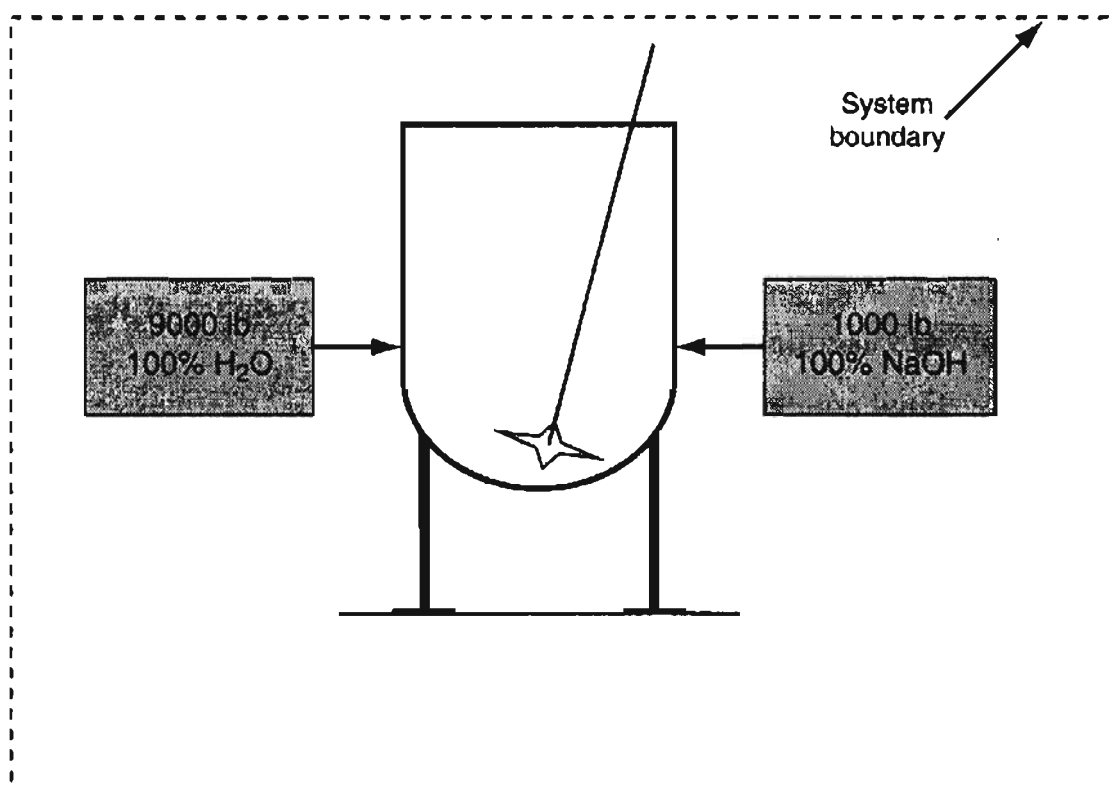


Figure 6.11a The initial state of a batch mixing process.

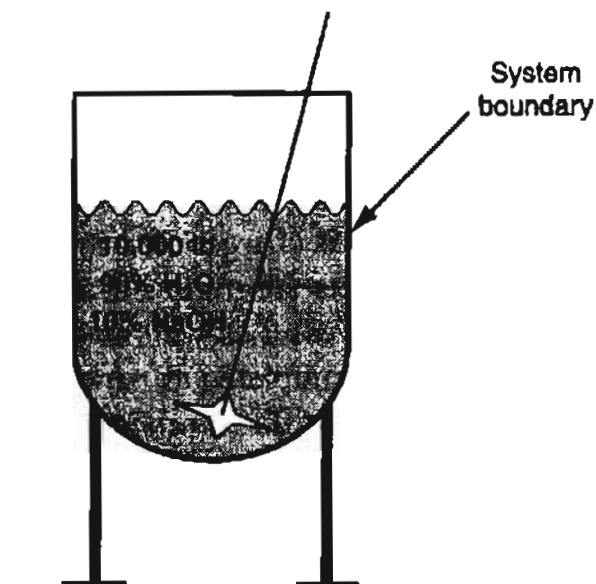


Figure 6.11b The final state of a batch mixing process.

are the same as the initial conditions. Chapter 28 treats the heating effect of the solution of NaOH in the H_2O .

Can you transform the analysis of a batch process, as shown in Figure 6.11, so that you can treat the system as an open flow system? You can if you take a different perspective of the process. Let us assume that the NaOH and H_2O are fed at nonconstant rates (all at once) into the system that contains zero initial material. Let us also assume that the product is removed at a nonconstant rate (all at once) so that the final conditions in the tank are the same as the initial conditions—nothing exists in the tank. Then the process represents an open system. Look at Figure 6.12. The inputs are the same as the initial amounts charged to the system. In Equation (6.4), the flows correspond to the accumulated total of the rates of flow over time, not the rates themselves. Hence, it is quite correct to imagine that the numerical values of the accumulated material are the same as the values that resulted from the instantaneous injection of NaOH and H_2O . Similar concepts apply to the output flow of the NaOH solution. We can summarize the hypothetical operation of the batch process as a flow system as follows:

Final conditions: All values = 0 Flows out:

NaOH = 1,000 lb
 H_2O = 9,000 lb
 Total = 10,000 lb

Initial conditions: All value = 0 Flows in:

NaOH = 1,000 lb
 H_2O = 9,000 lb
 Total = 10,000 lb

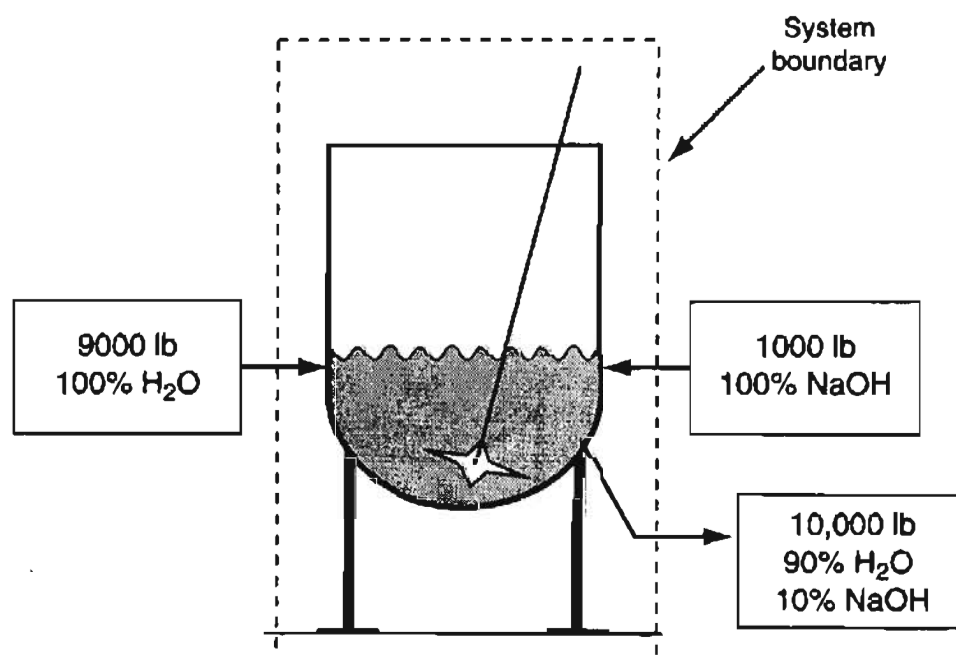


Figure 6.12 The batch process in Figure 6.11 represented as an open system.

In a **semi-batch process** material enters the process during its operation, but does not leave. Instead mass is allowed to accumulate in the process vessel. Product is withdrawn only after the process is over. Figures 6.13 illustrates a semi-batch mixing process. Initially the vessel is empty (Figure 6.13a). NaOH (1000 lb/hr) and H₂O (9000 lb/hr) are fed to the vessel, and the mixture (10% NaOH) accumulates in the vessel. Figure 6.13b shows the semi-batch system after 1 hour of operation. Semi-batch processes are open and unsteady-state.

Can you apply Equation (6.4) to a semi-batch system? Of course. Only flows enter the systems, and none leave, hence the system is an unsteady state—one that you can treat as having continuous flows, as follows:

Final conditions:

$$\text{NaOH} = 1,000 \text{ lb}$$

$$\text{H}_2\text{O} = \underline{9,000 \text{ lb}}$$

$$\text{Total} = 10,000 \text{ lb}$$

Initial conditions: All values = 0

Flows out: All values = 0

Flows in:

$$\text{NaOH} = 1,000 \text{ lb}$$

$$\text{H}_2\text{O} = \underline{9,000 \text{ lb}}$$

$$\text{Total} = 10,000 \text{ lb}$$

You can see that all of the numerical values we have been using in this section are the same. Only the perspective of how the values are classified with respect to the terms in Equation (6.4) discriminate among the analyses.

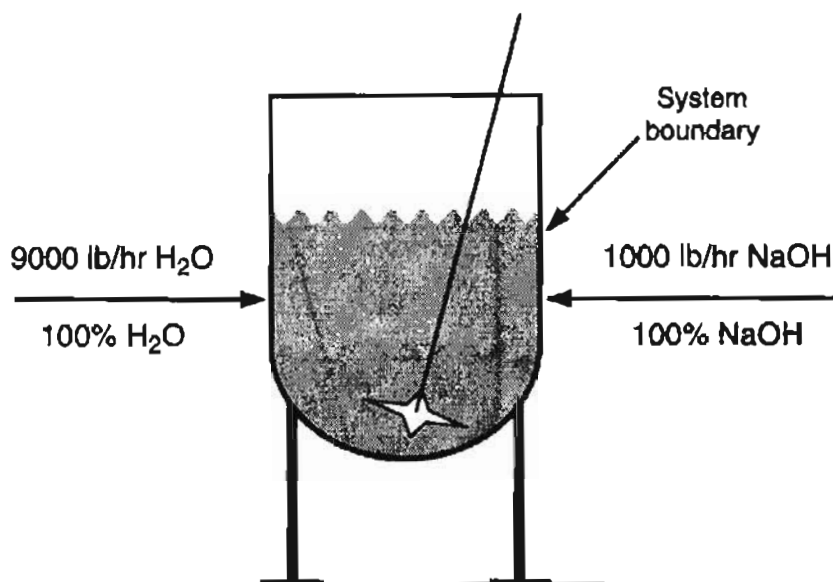


Figure 6.13a Initial condition for the semi-batch mixing process. Vessel is empty.

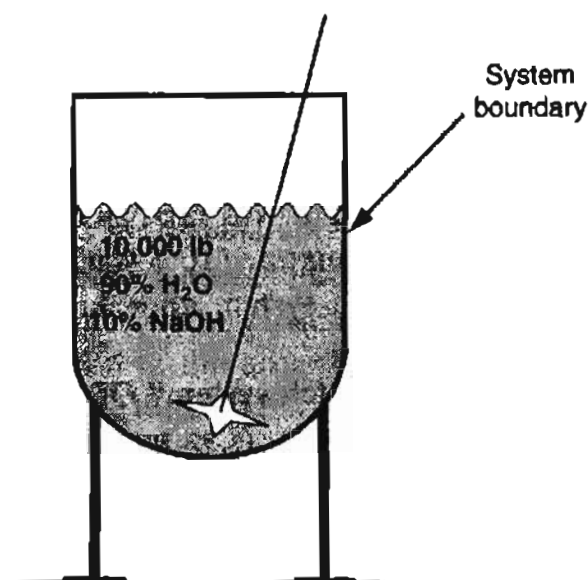


Figure 6.13b Condition of a semi-batch mixing process after 1 hour of operation.

EXAMPLE 6.3 Discharge of Tank Residuals to the Environment

Material lost in cleaning drums and tanks after their contents have been discharged not only represents economic loss but also possible environmental problems. After emptying, before tanks are flushed with water, a certain percent of the tank contents remains on the inside surface of the tank. A measurement for water flushing of a steel tank originally containing motor oil showed that 0.15 percent by weight of the original contents remained on the interior tank surface. What is the fractional loss of

oil before flushing with water, and the pounds of discharge of motor oil into the environment during cleaning of a 10,000 gal tank truck that carried motor oil.

Solution

Basis: 10,000 gal motor oil at an assumed 77°F

The density of motor oil is about 0.80 g/cm³. The initial mass of the motor oil in the tank was

$$\frac{10,000 \text{ gal}}{1 \text{ gal}} \left| \frac{0.1337 \text{ ft}^3}{1 \text{ gal}} \right| \left| \frac{62.4 \text{ lb water}}{1 \text{ ft}^3 \text{ water}} \right| \left| \frac{0.80 \text{ g/cm}^3 \text{ oil}}{1.00 \text{ g/cm}^3 \text{ water}} \right| = 66,700 \text{ lb}$$

The mass fractional loss is 0.0015. The oil material balance is

$$\begin{array}{rclcl} \text{Initial} & & \text{unloaded} & & \text{residual discharged on cleaning} \\ 66,700 & = & 66,700(0.9985) & + & 66,700(0.0015) \end{array}$$

Thus, the discharge on flushing is 66,700 (0.0015) = 100 lb.

SELF-ASSESSMENT TEST

Questions

1. What is the difference between a batch process and a closed process?
2. What is the difference between a semi-batch process and a closed process?
3. What is the difference between a semi-batch process and an open process?

Problems

1. Classify the following processes as (a) batch, (b) semi-batch, (c) neither, and (d) both:
 - a. a section of a river between two bridges
 - b. a home water heater
 - c. a reaction carried out in a beaker
 - d. preparing a pot of chili
 - e. water boiling in a pot on the stove
2. How would you proceed in the analysis of a steady-state system as an unsteady-state system?

Discussion Problem

1. How much time must elapse before a batch process becomes a semi-batch or open process?

Looking Back

In addition to introducing you to the concept of material balances, we covered some of the terminology that you will be using in solving material balance problems. The following list summarizes the types of material balances introduced in this chapter:

Total mass balance	Component mass balance
Total mole balance	Component mole balance

Other balances will be discussed in later chapters.

GLOSSARY OF NEW WORDS

Accumulation An increase or decrease in the material (e.g., mass or moles) in the system.

Batch process A process in which material is neither added to nor removed from the process during its operation.

Closed system A system that does not have material crossing the system boundary.

Component balance A material balance on a single chemical component in a system.

Conservation of mass Matter is neither created nor destroyed overall.

Consumption The depletion of a component in a system due to chemical reaction.

Continuous process A process in which material enters and/or exits continuously.

Final condition The amount of material (e.g., mass or moles) in the process at the end of the processing interval.

Flow system An open system with material entering and/or leaving.

Generation The appearance of a component in a system because of chemical reaction.

Initial condition The amount of a material (e.g., mass or moles) in the process at the beginning of the processing interval.

Input Material (e.g., mass, moles) that enters the system.

Material balance The balance equation that corresponds to the conservation of mass.

Negative accumulation A depletion of material (usually mass or moles) in the system.

Open system A system in which material crosses the system boundary.

Output Material (e.g., mass, moles) that leaves the system.

Rate Flow per unit time

Semi-batch process A process in which material enters the system but product is not removed during operation.

Steady-state system A system for which all the conditions (e.g., temperature, pressure, amount of material) remain constant with time.

System Any arbitrary portion of or whole process that is considered for analysis.

System boundary The closed line that encloses the portion of the process that is to be analyzed.

Transient system A system for which one or more of the conditions (e.g., temperature, pressure, amount of material) of the system vary with time. Also known as an unsteady-state system.

Unsteady-state system A system for which one or more of the conditions (e.g., temperature, pressure, amount of material) of the system vary with time. Also known as a transient system.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent:

CACHE Corp. *Material and Energy Balances 2.0* (CD), Austin, TX (2000).

Fogler, H. S., and S. M. Montgomery. *Interactive Computer Modules for ChE. Instruction*, CACHE Corp., Austin, TX (2000).

Veverka, V. V., and F. Madron. *Material and Energy Balances in the Process Industries: From Microscopic Balances to Large Plant*, Elsevier Science, Amsterdam (1998).

Web Sites

http://www.outokumpu.fi/hsc/whats_new_heat.htm

<http://voyager5.sdsu.edu/testcenter/features/cgprocess/index>

www.chemeng.ed.ac.uk/~jwp/MSO/section1/balance.html

Answer to the puzzle

The additions and subtractions made in the puzzle are invalid. A diagram of the flow of money shows the transfers (amounts on the arrows) and final conditions (the amounts within the boxes):

You can see that the money balance should be made for the net results among the five individuals in the boxes, and not of flows between the boxes:

$$\$55 + \$2 - (\$19)(3) = 0$$

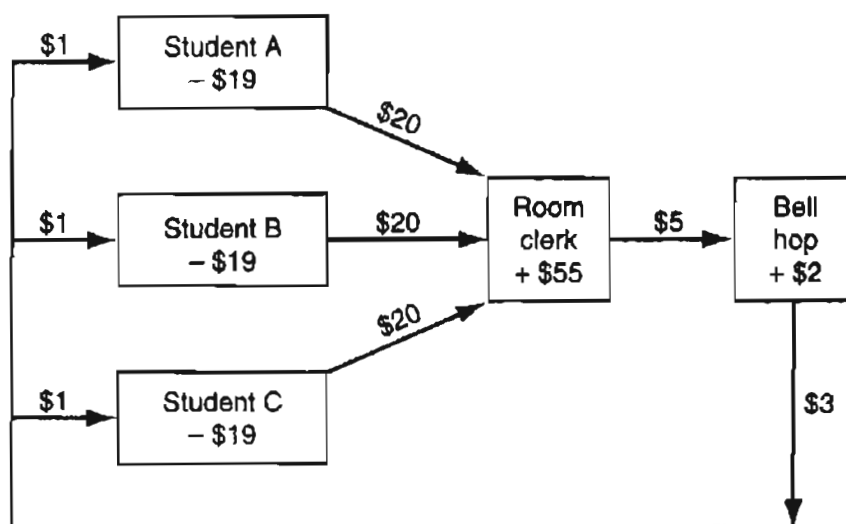


Figure 6.14

PROBLEMS

- *6.1 A manufacturer blends lubricating oil by mixing 300 kg/min of No. 10 oil with 100 kg/min of No. 40 oil in a tank. The oil is well mixed, and is withdrawn at the rate of 380 kg/min. Assume the tank contains no oil at the start of the blending process. How much oil remains in the tank after one hour?
- *6.2 One hundred kg of sugar are dissolved in 500 kg of water in a shallow open cylindrical vessel. After standing for 10 days, 300 kg of sugar solution are removed. Would you expect the remaining sugar solution to have a mass of 300 kg?
- *6.3 A 1.0-gram sample of solid iodine is placed in a tube and the tube is sealed after all of the air is removed. The tube and the solid iodine together weigh 27.0 grams.

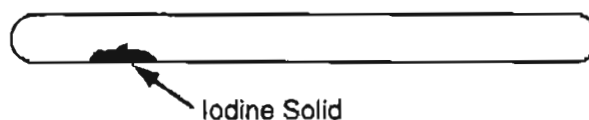


Figure P6.3

The tube is then heated until all of the iodine evaporates and the tube is filled with iodine gas. The weight after heating should be:

- (a) less than 26.0 grams.
 - (b) 26.0 grams.
 - (c) 27.0 grams.
 - (d) 28.0 grams.
 - (e) more than 28.0 grams.
- ✓ *6.4 Mixers can be used to mix streams with different compositions to produce a product stream with an intermediate composition. Figure P6.4 shows a diagram of such a mixing process. Evaluate the closure of the overall material balance and the component material balances for this process. Closure means how closely the inputs agree with the outputs for a steady state process.

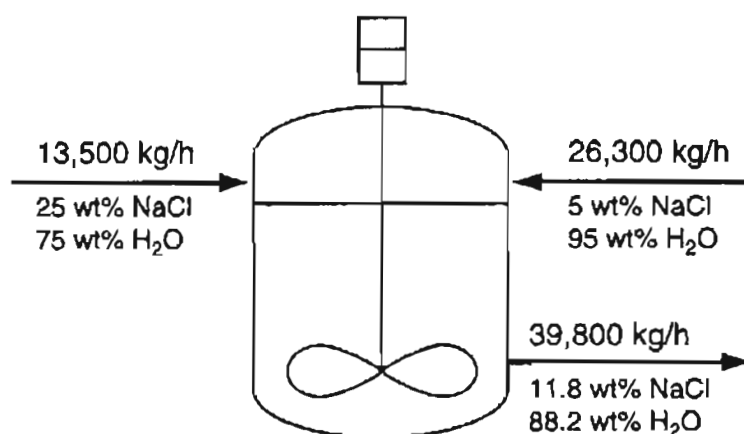


Figure P6.4

- *6.5** Heat exchangers are used to transfer heat from one fluid to another fluid, such as from a hotter fluid to a cooler fluid. Figure P6.5 shows a heat exchanger that transfers heat from condensing steam to a process stream. The steam condenses on the outside of the heat exchanger tubes while the process fluid absorbs heat as it passes through inside of the heat exchanger tubes. The feed rate of the process stream is measured as 45,000 lb/h. The flow rate of steam is measured as 30,800 lb/h, and the exit flow rate of the process stream is measured as 50,000 lb/h. Perform a mass balance for the process stream. If the balance does not close adequately, what might be a reason for this discrepancy?

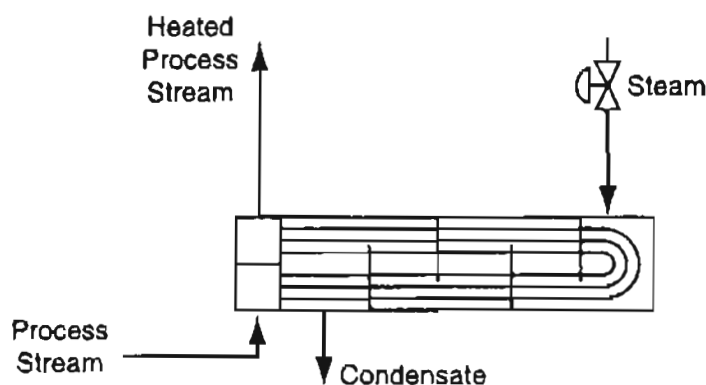


Figure P6.5

- *6.6** Distillations columns are used to separate light boiling components from heavier boiling components, and make up over 95% of the separation systems for the chemical process industries. A commonly used distillation column is a propylene-propane splitter. The overhead product from this column is used as a feedstock for the production of polypropylene, which is the largest quantity of plastic produced worldwide. Figure P6.6 shows a diagram of a propylene-propane splitter (C_3 refers to propane and $C_3^=$ refers to propylene). The steam is used to provide energy, and is not involved in the process material balance). Assume that the composition and flow rates listed on this diagram came from process measurements. Determine if the overall material balance is satisfied for this system. Evaluate the component material balances as well. What can you conclude?

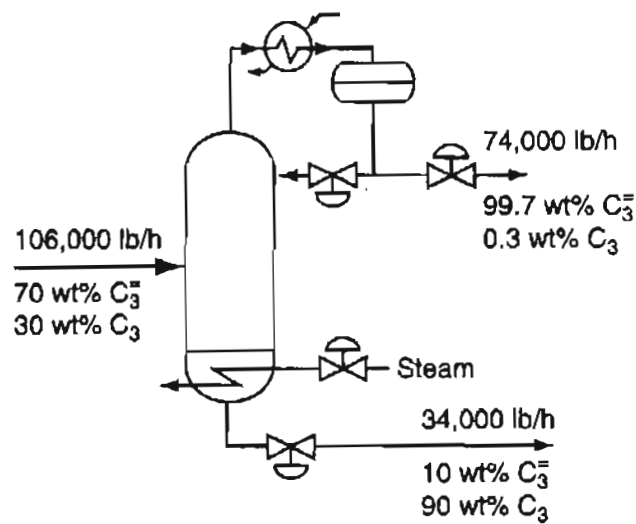


Figure P6.6

- **6.7** Examine the flow sheet in Figure P6.7 (adapted from *Hydrocarbon Processing*, November 1974, p. 159) for the atmospheric distillation and pyrolysis of all atmospheric distillates for fuels and petrochemicals. Does the mass in equal the mass out? Give one or two reasons why the mass does or does not balance. Note: T/A is metric tons/year.

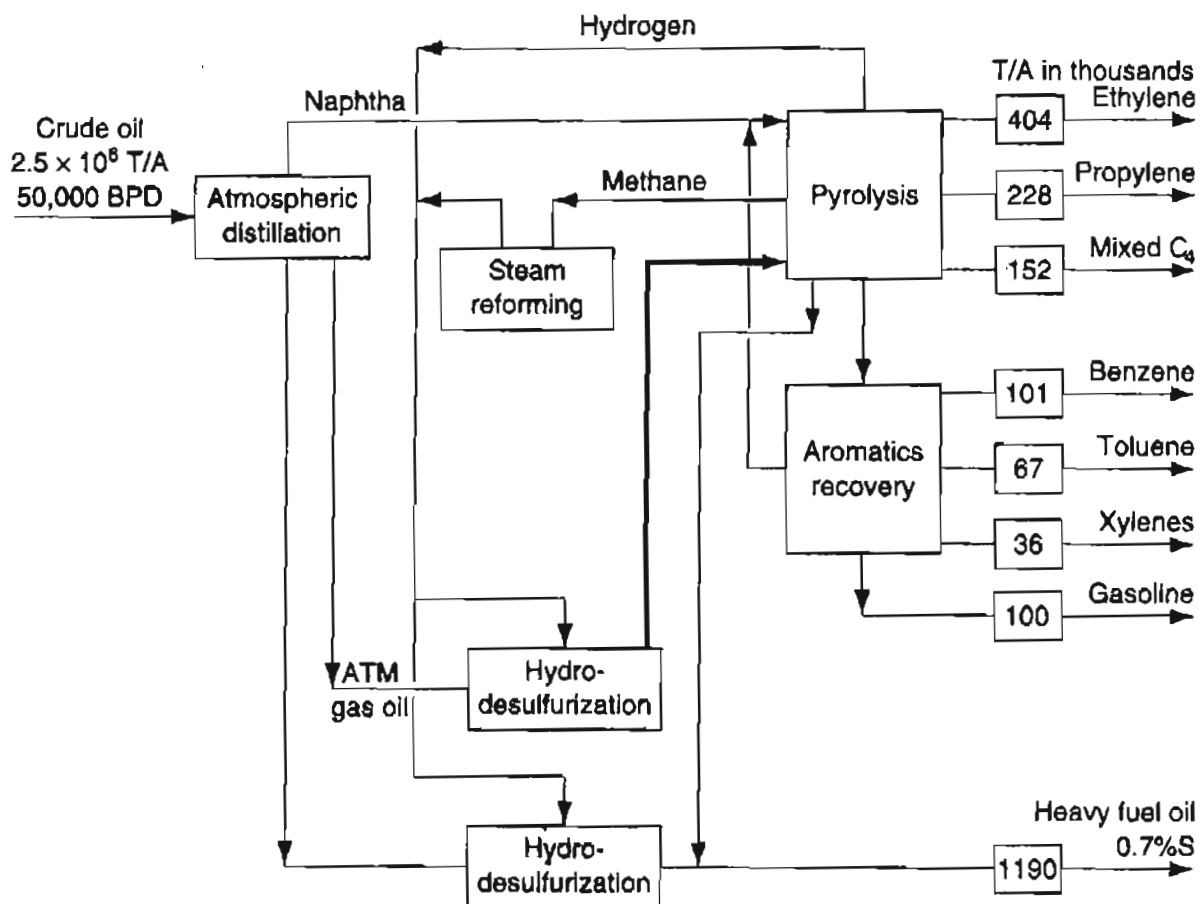


Figure P6.7

- **6.8** Examine the flow sheet in Figure P6.8. Does the mass in equal the mass out? Give one or two reasons why the mass does or does not balance.

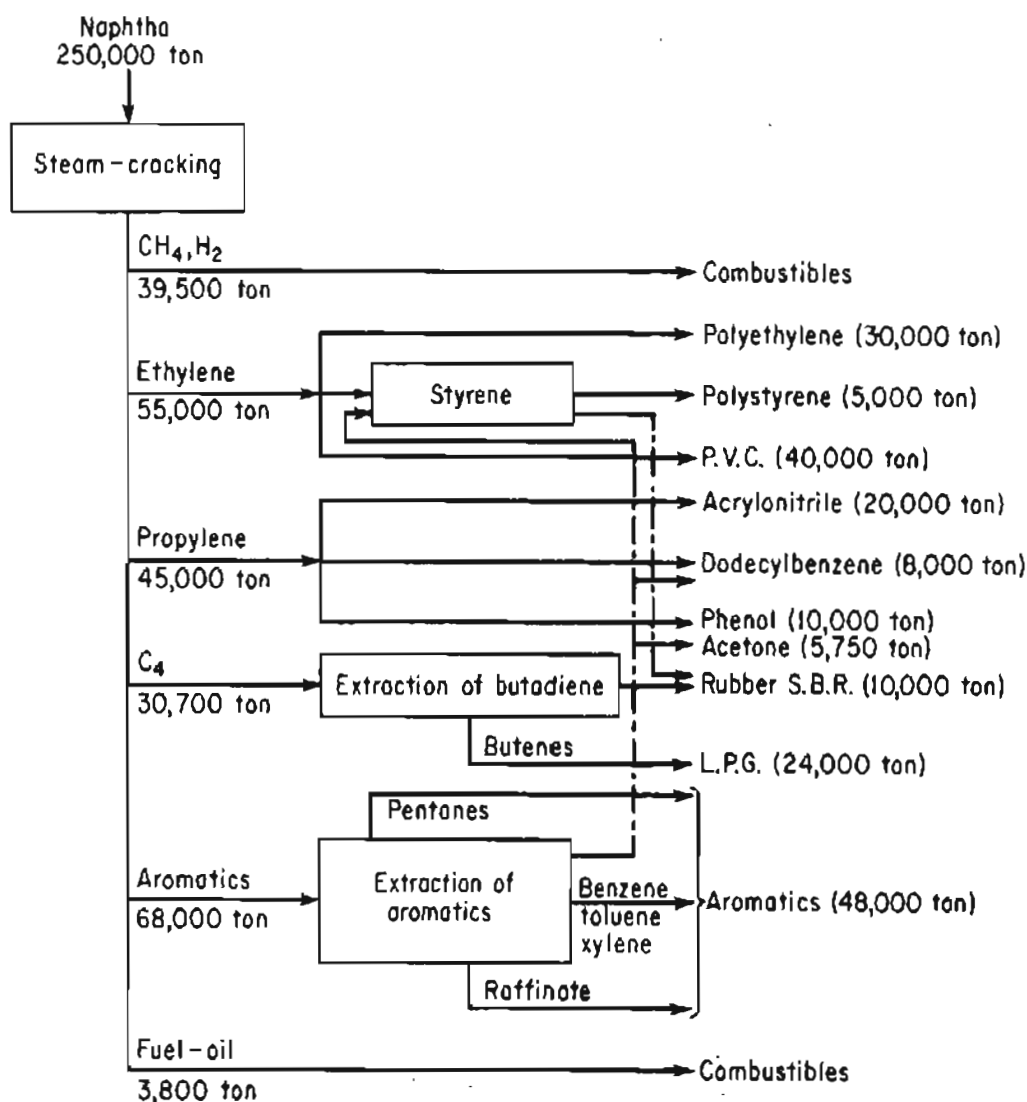


Figure P6.8

- **6.9** Examine Figure P6.9. Is the material balance satisfactory? (T/wk means tons per week)
- *6.10** Examine Figure P6.10 (adapted from *Environ. Sci. Technol.*, 27 (1993, p. 1975). What would be a good system to designate for this bioremediation process? Sketch the process and draw the system boundary. Is your system open or closed? Is it steady state or unsteady state?
- *6.11** Examine Figure P6.11 of a cylinder that is part of a Ford 2.9 liter V-6 engine. Pick a system and state it.

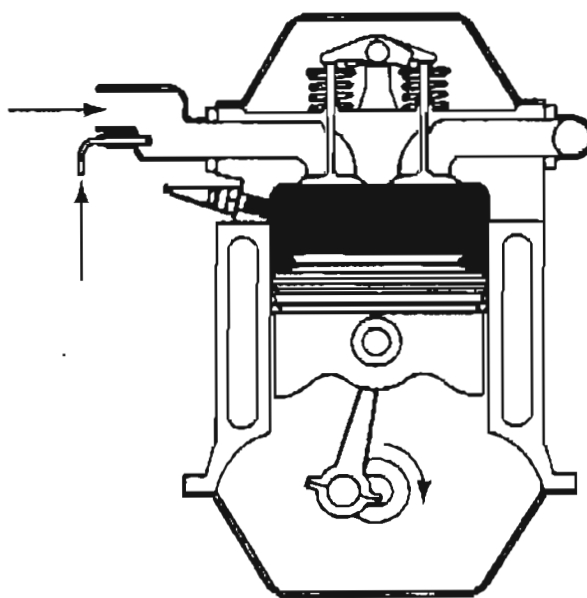


Figure P6.11

- Show by a crude sketch the system boundary. State whether your system is a flow system or a batch system and why (in one sentence).
- *6.12** State whether the following processes represent open or closed systems in making material balances.
- The global carbon cycle of the earth.
 - The carbon cycle for a forest.
 - An outboard motor for a boat.
 - Your home air conditioner with respect to the coolant.
- *6.13** Read each one of the following scenarios. State what the system is. Draw the picture. Classify each as belonging to one or more of the following: open system, closed system, steady-state process, unsteady-state process.
- You fill your car radiator with coolant.
 - You drain your car radiator.
 - You overfill the car radiator and the coolant runs on the ground.
 - The radiator is full and the water pump circulates water to and from the engine while the engine is running.
- *6.14** State whether the following processes represent open or closed systems, and explain your answer very briefly.
- swimming pool (from the view point of the water)
 - home furnace
- *6.15** State whether the process of a block of ice being melted by the sun (system the ice) is an open or closed system, batch or flow, and steady state or unsteady state. List the choices in a *vertical* list, and state beside each entry any assumption you make.

***6.16** Examine the processes in Figure P6.16. Each box represents a system. For each, state whether:

- (a) The process is in the
 - (1) steady state,
 - (2) unsteady state, or
 - (3) unknown condition
- (b) The system is
 - (1) closed,
 - (2) open,
 - (3) neither, or
 - (4) both

The wavy line represents the initial fluid level when the flows begin. In case (c), the tank stays full.

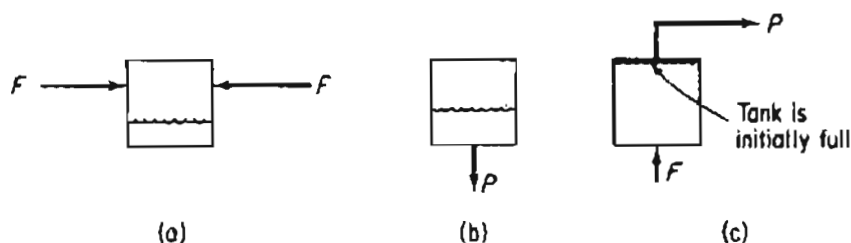


Figure P6.16

***6.17** Pick the correct answer(s):

For a steady state system

- (a) The rate of input is zero
- (b) The rate of generation is zero
- (c) The rate of consumption is zero
- (d) The rate of accumulation is zero

***6.18** Consider a hot water heater in a house. Assume that the metal shell of the tank is the system boundary.

- (a) What is in the system?
- (b) What is outside the system?
- (c) Does the system exchange material with the outside of the system?
- (d) Could you pick another system boundary?

***6.19** Explain why the total moles entering a process may not equal the total moles leaving.

✓***6.20** Silicon rods used in the manufacture of chips can be prepared by the Czochralski (LEC) process in which a cylinder of rotating silicon is slowly drawn from a heated bath. Examine Fig. P6.20. If the initial bath contains 62 kg of silicon, and a cylindrical ingot 17.5 cm in diameter is to be removed slowly from the melt at the rate of 3 mm per minute, how long will it take to remove one-half of the silicon? What is the accumulation of silicon in the melt?

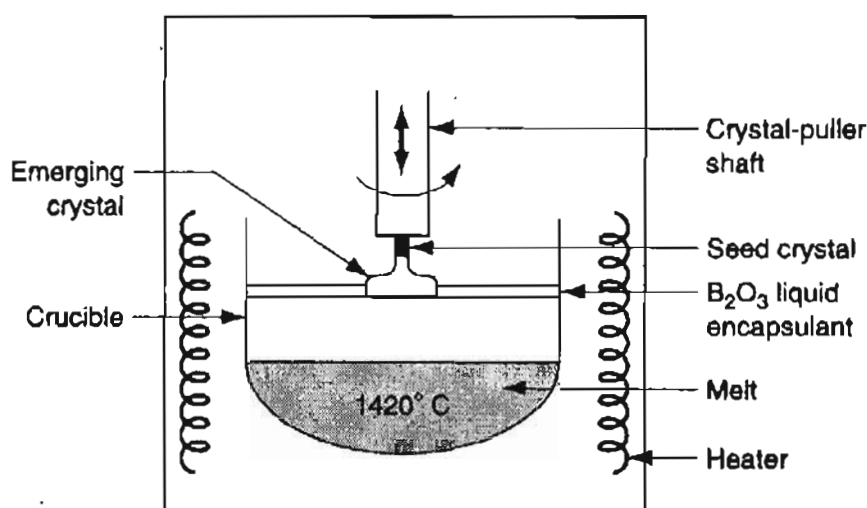


Figure P6.20

- *6.21 A thickener in a waste disposal unit of a plant removes water from wet sewage sludge as shown in Figure P6.21. How many kilograms of water leave the thickener per 100 kg of wet sludge that enter the thickener? The process is in the steady state.

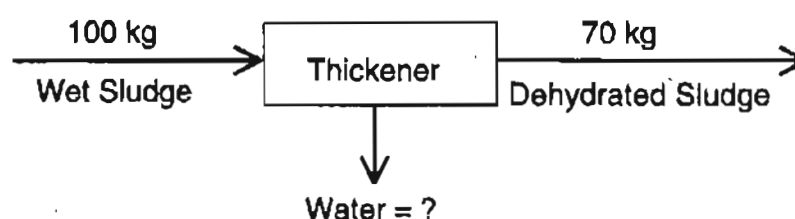


Figure P6.21

- *6.22 In making a material balance, classify the following processes as (a) batch, (b) semi-batch, (c) continuous, (d) open or flow, (e) closed, (f) unsteady state, or (g) steady state. More than one classification may apply.
1. A tower used to store water for a city distribution system
 2. A can of soda
 3. Heating up cold coffee
 4. A flush tank on a toilet
 5. An electric clothes drier
 6. Waterfall
 7. Boiling water in an open pot
- *6.23 Under what circumstances can a batch process that is carried out repeatedly be considered to be a continuous process?
- *6.24 How long a time should elapse before a batch or semi-batch process can be considered an open process?

CHAPTER 7

A GENERAL STRATEGY FOR SOLVING MATERIAL BALANCE PROBLEMS

7.1 Problem Solving

167

7.2 The Strategy for Solving Problems

168

Your objectives in studying this chapter are to be able to:

1. Comprehend and execute the 10 elements of effective problem solving.
2. Understand and apply a degree of freedom analysis.

The difference between the almost right strategy and the right strategy is really a large matter—it's the difference between a lightning bug and lightning.

A paraphrase of Mark Twain

What is the purpose of having a chapter that discusses how to solve material balance problems? The idea is to provide you with guidelines so that you can be efficient and effective in solving material balance problems. If you begin to apply the suggested strategy at once, as you proceed through this book you will discover by the end that you have become quite skilled at problem solving. If you get stuck in solving a problem or bungle it, you can rebound and recover by applying the proposed strategy. If you are going to learn from your mistakes, let's find out what they are first.

Looking Ahead

This chapter presents a comprehensive methodology that you can use to solve material balance problems. We are going to describe a strategy of analysis that will help you understand, first, how similar material balance problems are, and second,

how to solve them in the most expeditious manner. You do not have to memorize the strategy. If you consistently use it in developing your skills, you will learn it by absorption.

7.1 Problem Solving

Most of the literature on problem solving view a “problem” as a gap between some initial information (the initial state) and the desired information (the final state). Problem solving is the activity of closing the gap between these two states. If you are going to become a professional, you will have to acquire a number of skills in problem solving such as:

- formulating specific questions from vaguely specified problems;
- selecting effective problem-solving strategies;
- deciding when an estimate will suffice versus an exact answer;
- using tables, graphs, spreadsheets, calculators, and computers to organize, solve, and interpret the results from solving problems;
- judging the validity of the work of others; and
- evaluating answers.

You will find as you go through this book that routine substitution of data into an appropriate equation will not be adequate to solve material (and energy) balances other than the most trivial ones. You can, of course, formulate your own strategy for solving problems—everyone has a different viewpoint. But adoption of the well-tested general strategy presented in this chapter has been found to significantly ease the difficulty students have when they encounter problems not exactly the same as those presented as examples and homework in this book, or problems in industrial practice. After all, the problems in this book are only samples, and simple ones at that, of the myriad of problems that exist or could be formulated.

An orderly method of analyzing problems and presenting their solutions represents training in logical thinking that is of considerably greater value than mere knowledge of how to solve a particular type of problem. Understanding how to approach these problems from a logical viewpoint will help you to develop those fundamentals of thinking that will assist you in your work as an engineer long after you have read this material. Keep in mind the old Chinese proverb:

None of the secrets of success will work unless you do.

When solving problems, either academic or industrial, you should always use “engineering judgment” even though much of your training to date treats problems

as an exact science. For instance, suppose that it takes one man 10 days to build a brick wall; then 10 men can finish it in one day. Therefore, 240 men can finish the wall in 1 hr, 14,400 can do the job in 1 min, and with 864,000 men the wall will be up before a single brick is in place! Your password to success is to use some common sense in problem solving and always maintain a mental picture of the system that you are analyzing. Do not allow a problem to become abstract and unrelated to physical behavior.

7.2 The Strategy for Solving Problems

Howe's Law: Every person has a scheme that will not work.

Gordon's Law: If a project is not worth doing, it is not worth doing well.

You neither have to follow the steps in the list below in any particular sequence nor formally employ every one of them. You can go back several steps and repeat steps at will. As you might expect, when you work on solving a problem you will experience false starts, encounter extensive preliminary calculations, suspend work for higher priority tasks, look for missing links, and make foolish mistakes. The strategy outlined below is designed to focus your attention on the main path rather than the detours.

1. Read and understand the problem statement

This means **read the problem carefully** so that you know what is given and what is to be accomplished. Rephrase the problem to make sure you understand it. An anecdote illustrates the point of really understanding the problem:

An English family visiting Khartoum in the Sudan took their young son each day by the statue of General Gordon on a camel. On the last day of their visit to the statue as the family was leaving, the boy asked, "Who was that man sat on General Gordon?"

Here is a question to answer:

How many months have 30 days?

Now you may remember the mnemonic: 30 days hath September . . . and give the answer as four, but is that what the question concerns—how many months have exactly 30 days? Or, does the question ask how many months have at least 30 days (with the answer being 11)?

Be sure to decide if a problem is just some simple calculation or involves a steady-state or unsteady-state process, and state your assumption at the top of your calculation page.

EXAMPLE 7.1 Understanding the Problem

A train is approaching the station at 105 cm/s. A man in one car is walking forward at 30 cm/s relative to the seats. He is eating a foot-long hot dog, which is entering his mouth at the rate of 2 cm/s. An ant on the hot dog is running away from the man's mouth at 1 cm/s. How fast is the ant approaching the station? Cover up the solution below, and try to determine what the problem requests before peeking.

Solution

As you read the problem make sure you understand how each piece of information meshes with the others. Would you agree that the following is the correct analysis?

A superficial analysis would take care to ignore the hot dog length but would calculate: $105 + 30 - 2 + 1 = 134$ cm/s for the answer. However, the problem states on more careful reading that the ant is moving away from the man's mouth at the rate of 1 cm/s. Because the man's mouth is moving toward the station at the rate of 135 cm/s, the ant is moving toward the station at the rate of 136 cm/s.

2. Draw a sketch of the process and specify the system boundary

In Chapter 2 we showed how a process can be represented by simple diagrams, and you have seen numerous diagrams of processes in subsequent chapters. It is always good practice to begin solving a problem by drawing a sketch of the process or physical system. You do not have to be an artist to make a sketch. A simple box or circle drawn by hand to denote the system boundary with some arrows to designate flows of material will be fine. You can also state what the system is in words or by a label.

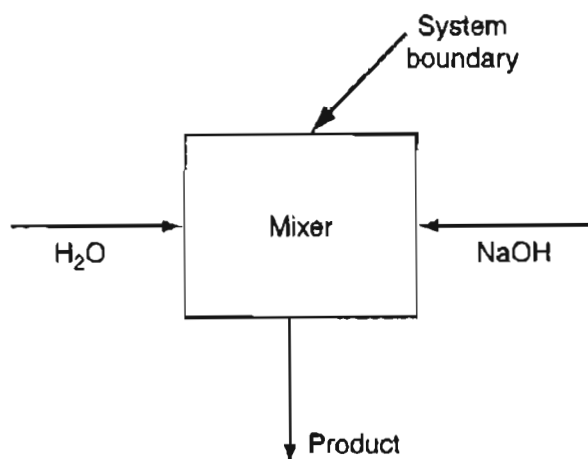
EXAMPLE 7.2 Drawing a Sketch of a Mixing Process

A continuous mixer mixes NaOH with H₂O to produce an aqueous solution of NaOH. Determine the composition and flow rate of the product if the flow rate of NaOH is 1000 kg/hr, and the ratio of the flow rate of the H₂O to the product solution is 0.9.

We will use this example in subsequent illustrations of the proposed strategy. For this example, just a sketch of the process is required.

Solution

The process is an open one, and we assume it to be steady state (nothing specific is mentioned in the problem statement, but steady state is implied). We pick the mixer as the system. The diagram below probably looks nicer than one you would draw by hand.

**Figure E7.2**

3. Place labels (symbols, numbers, and units) on the diagram for all of the known flows, materials, and compositions. For the unknown flows, materials, and compositions insert symbols and units. Add any other useful relations or information.

By putting data on the diagram you will avoid having to look back at the problem statement repeatedly, and you will also be able to clarify what data are missing. What kinds of information might you place on the diagram? Some specific examples of information that you might put on the diagram are:

- Stream flow rates ($F = 100 \text{ kg/min}$)
 - Compositions of each stream ($x_{\text{H}_2\text{O}} = 0.40$)
 - Given flow ratios ($F/R = 0.7$)
 - Given identities ($F = P$)
 - Yields ($Y \text{ kg}/X \text{ kg} = 0.63$)
 - Efficiency (40%)
 - Specifications for a variable or a constraint ($x < 1.00$)
 - Conversion (78%)
 - Equilibrium relationships ($y/x = 2.7$)
 - Molecular weights ($\text{MW} = 129.8$)
- } the essential information

How much data should you place on the diagram? Enough to solve the problem and interpret the answer. If your diagram becomes too crowded with data, make a separate table and key it to the diagram. **Be sure to include the units associated with the flows and other material when you write the numbers on your diagram or in a table. The units make a difference in your thought processes.**

Some of the essential data may be missing from the problem statement. If you do not know the value of a variable to put on the figure, you can substitute a symbol such as F_1 , F_1 , or F^1 for an unknown flowrate or x_1 for a mole fraction. Substitution of a symbol for a number will focus your attention on searching for the appropriate information needed to solve the problem.

EXAMPLE 7.3 Placing the Known Information on the Diagram

For the problem stated in Example 7.2, place the known information on the diagram of the process.

Solution

Because no contrary information is provided about the composition of the H_2O and NaOH streams, we will assume that they are 100% H_2O and NaOH , respectively. Look at Figure E7.3 for a typical way the data might be put on a diagram.

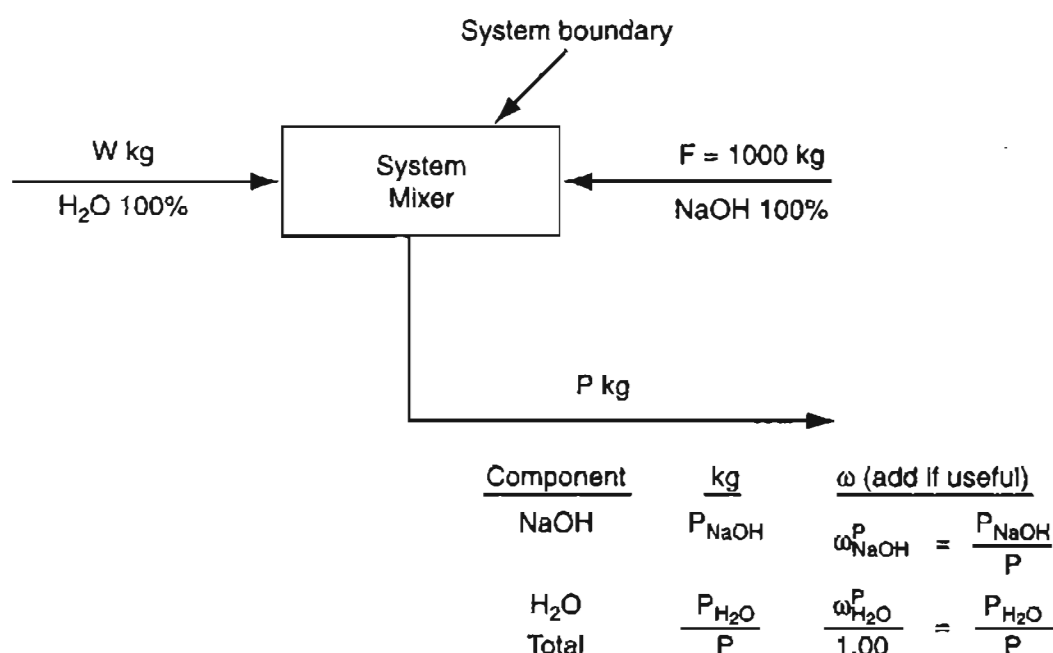


Figure E7.3

Note that the composition of the product stream is listed along with the symbols for unknown flows. Could you have listed the mass fractions instead of or in addition to the mass flows? Of course. Look to the right of the column headed "kg." Because you know the ratio $W/P = 0.9$, why not add that ratio to the diagram at some convenient place?

You will find it convenient to use a consistent set of algebraic symbols to represent the variables whose values are unknown (called the **unknowns**) in a problem. In this book we frequently use mnemonic letters to represent the flow of material, both mass and moles, with the appropriate units attached or inferred, as illustrated in Figure E7.3. By flow we mean a certain amount of material, not a rate of flow (that involves time). A rate of flow is denoted by an overlay dot, such as \dot{F} . We usually employ m for the flow of mass and n for the flow of moles with appropriate subscripts and/or superscripts to make the meaning crystal clear. Table 7.1 lists some examples. You can use any symbols you want, but it helps to be consistent. In specific problems pick obvious or mnemonic letters such as W for water and P for product to avoid confusion. If you run out of suitable letters of the alphabet, you can always insert superscripts to distinguish between streams such as F^1 from F^2 , or label streams as $F1$ and $F2$.

In the beginning there was the symbol.

David Hilbert

TABLE 7.1 Some Examples of the Symbols Used in This Book

Symbol	Designates
F kg	Flow of mass in kg
F_{Total} or F_{Tot}	Total flow of material*
F^1 or $F1$	Flow in stream number 1*
F_A lb	Flow of component A in stream F in lb
m_A	Mass flow of component A*
m_{Total} or m_{Tot}	Mass flow of the total material*
m_A^{F1}	Mass flow of component A in stream $F1$ *
n_A^W	Molar flow of component A in stream W *
ω_A^F	The mass (weight) fraction of A in stream F . (The superscript is not required if the meaning is otherwise clear.)
x_A^F	The mole fraction of A in stream F , a liquid. (The superscript is not required if the meaning is otherwise clear.)
y_A^F	The mole fraction of A in stream F , usually a gas.

*Units not specified but inferred from the problem statement.

4. Obtain any data you need to solve the problem, but are missing*Never assume the obvious is true*William Safire in the *Sleeping Spy* (Random House)

An evaporator costs \$34,700. How much did it cost per pound? Clearly, something is missing from the problem statement. Table 7.2 is a clever list of the degrees of ignorance. Look at Table 7.2 and decide what your level of ignorance is for the evaporator problem. Did you pick Level 1? Hopefully you are not at Level 2! You have to find out what the weight (mass) of the evaporator is.

TABLE 7.2 Armour's Laws of Ignorance
(P.G. Armour, *Commun. ACM*, 44, 15 (2001))

Order of Ignorance		State of Mind
0	Lack of ignorance	You know something
1	Lack of knowledge	You don't know something
2	Lack of awareness	You don't know that you don't know something
3	Lack of process	You don't know an efficient way to find out that you don't know that you don't know something.
4	Meta-ignorance	You don't know about the five orders of ignorance.

Another example is: How do you pronounce the name of the capital of Kentucky: "Loo-EE-ville" or "Loo-ISS-ville"? If you pick either one you have demonstrated ignorance at Level 2! Hint: Look at a map.

When you review a problem, you may immediately notice that some essential detail, such as a physical property (molecular weight, density, etc.), is missing in the problem statement. You can look the values up in a physical properties database such as the one on the CD that accompanies this book, in reference books, on the Web, and many other places. Or some value may be missing, but you can calculate the value in your head. For example, you are given a stream flow that contains just two components, one is H_2O and the other $NaOH$. You are given the concentration of the $NaOH$ as 22%. There is no point in writing down a symbol on the diagram for the unknown concentration of water. Why not just calculate the value of 78% in your head, and put that value on the diagram.

5. Choose a basis

We discussed the topic of basis in Chapter 3 where we suggested three ways of selecting a basis:

- (1) What do I have
- (2) What do I want to find,
- (3) What is convenient

Although picking a basis is Step 5 in the proposed strategy, frequently you know what basis to pick immediately after reading the problem statement, and can enter the value on your calculation page at that time. What basis would you choose for the problem stated in Example 7.2? Wouldn't you pick one of the following (all are equivalent)?

1000 kg

1 hour

1000 kg/hr

Whether you make the material balance in terms of mass (or moles), or in terms of a rate, namely mass (or moles) per unit time, makes no essential difference. Mass (or moles) is balanced. If you use a rate for the balance, you do have to carry along the dangling time unit in the equations.

Be sure to write the word *Basis* on your calculation page, and enter the value and associated units so that you, and anyone who reads the page, can later know what you did.

6. Determine the number of variables whose values are unknown (the *unknowns*)

Plan ahead

Unknown

If you put symbols on the process diagram as described in Steps 2, 3, and 4 above, or make a list of them, determining the number of unknowns is easy. Count them. In the problem stated in Example 7.2 from which Figure E7.3 was prepared, how many unknowns exist? We do not know the values of four variables: W , P , P_{NaOH} , and $P_{\text{H}_2\text{O}}$. In light of the necessary conditions stated in the next step, Step 7, you should be thinking about assembling four independent equations to solve the mixing problem.

7. Determine the number of independent equations and carry out a degrees of freedom analysis

Traveling through a maze looks easy from above.

IMPORTANT COMMENT

Before proceeding with Step 7, we need to call to your attention an important point from mathematics related to solving equations. Steps 6 and 7 focus on determining whether you can actually solve a set of equations formulated for a material

balance problem. For simple problems, if you omit Steps 6 and 7 and proceed directly to Step 8 (writing equations), you probably will not encounter any difficulties. However, for complicated problems, you can easily run into trouble if you neglect the two steps. Computer-based process simulators take great care to make sure that the equations you formulate indeed can be solved.

What does solving a material balance problem mean? For our purposes it means finding a unique answer to a problem. If the material balances you write are linear equations (refer to Appendix L if you are not clear as to what linear equation means) as will be the vast majority of the equations you write, then you are guaranteed to get a unique answer if the following necessary conditions are fulfilled:

The number of variables whose values are unknown equals the number of independent equations you formulate to solve a problem.

To check the sufficient conditions for this guarantee, refer to Appendix L.

Frequently Asked Questions

1. What does the term *independent equations* mean? You know that if you add two equations together to get a third one, the set of three equations is said to be *not independent*; they are said to be *dependent*. Only two of the equations are said to be independent because you can add or subtract any two of them to get the third equation. For example, you can determine by inspection that the two equations

$$3x_1 + 4x_2 = 0$$

$$x_1 - 3x_2 = 0$$

are independent. However, the following two equations

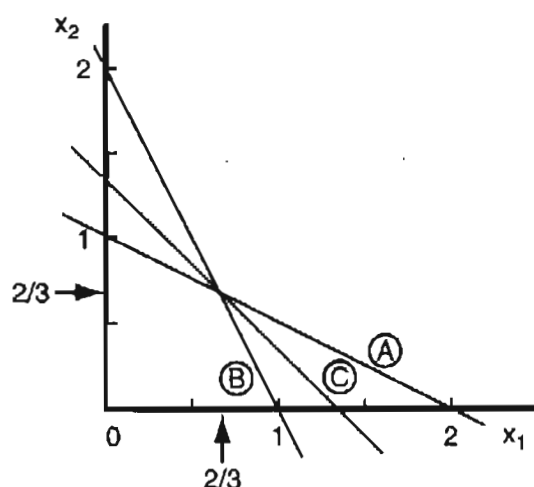
$$3x_1 + 4x_2 = 0$$

$$6x_1 + 8x_2 = 0$$

are not independent (as you can tell by inspection). Consult Appendix L1 for a formal definition of independence.

2. If I have several equations, how can I tell if they are independent? The best thing to do is use a software program to make the calculations. Matlab, MathCad, Mathematica, Excel, and many statistical programs will do the task for you. For information as to how to use software to determine whether or not equations are independent, refer to Appendix L1.

The concept of independence of equations will become clear if you look at Figure 7.1, which shows a set of three equations, only two of which are independent.



- (A) $x_1 + 2x_2 = 2$
 (B) $2x_1 + x_2 = 2$
 (C) $3x_1 + 3x_2 = 4$

Figure 7.1 An example of three equations intersecting at a unique solution. Only two of the equations are independent.

Note that in Figure 7.1 Equation (C) is the sum of Equations (A) and (B). Thus, although the three equations give a unique solution, only two can be counted as independent equations, and *any* two can be solved to get the unique solution. For the problem posed in Example 7.2 you can write three material balances:

- one for the NaOH
- one for the H_2O
- one total balance (the sum of the two component balances)

Only two are independent. You can use any combination of two of the three in solving the problem.

If you are not careful, you can blunder and write independent equations that have no joint solution. Look at Figure 7.2. Refer to Appendix L1 for a way to detect such a case. If you are careful in writing the component balances and selecting additional constraints, you will not be bothered by the difficulty illustrated in Figure 7.2.

In Step 7 you want to *preview* the compilation of equations you plan to use to solve the problem. You want to make sure that you have an appropriate number of independent equations. What kinds of equations should you be thinking about? The first class of equations to consider, of course, contains the material balances. **You can write as many independent material balances as there are species involved in the system.** In the specific case of the problem stated in Example 7.2, you have two species, NaOH and H_2O , and can thus

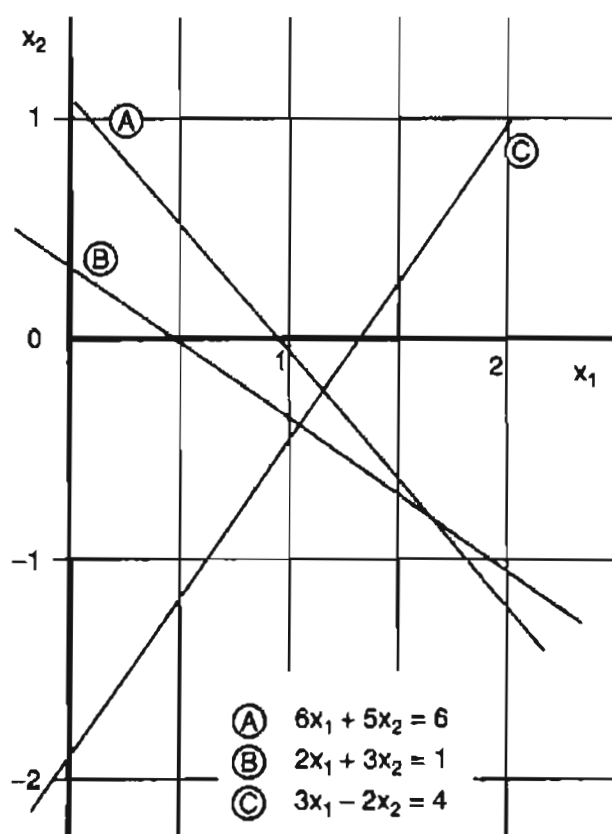


Figure 7.2 Three independent equations having no unique solution.

write two independent equations. Step 8 pertains to actually writing the equations, but you can write them down as you name them if you want.

In addition to the two species balances, to solve the problem posed in Example 7.2 you will need to find two more equations. In general you look for relations such as

- explicit relations specified (the **specifications**) in the problem statement such as $W/P = 0.9$ stated in Example 7.2
- implicit relations, particularly the sum of the mass or mole fractions being unity in a stream; in Example 7.2 you have

$$\omega_{\text{NaOH}}^P + \omega_{\text{H}_2\text{O}}^P = 1$$

or, multiplying both sides of the equation by P (the given amount of material) you get the equivalent equation

$$P_{\text{NaOH}} + P_{\text{H}_2\text{O}} = P$$

- specified values of variables that are given in the problem statement
- the value of the basis you select.

Once you have determined the number of unknowns and independent equations, an analysis of whether a problem is solvable or not is called a

degree-of-freedom analysis. The phrase *degrees of freedom* has evolved from the design of plants in which fewer independent equations than unknowns exist. The difference is called the degrees of freedom available to the designer to specify flow rates, equipment sizes, and so on. You calculate the number of degrees of freedom (N_D) as follows:

Degrees of freedom = number of unknowns – number of independent equations

$$N_D = N_U - N_E$$

When you calculate the number of degrees of freedom you ascertain the solvability of a problem. Three outcomes exist:

Case	N_D	Possibility of a solution
$N_U = N_E$	0	Exactly specified (determined); a solution exists
$N_U > N_E$	>0	Underspecified (determined); more independent equations required
$N_U < N_E$	<0	Overspecified (determined); in general no solution exists unless some constraints are eliminated or some additional unknowns are included in the problem

For the problem in Example 7.2,

$$\text{From Step 6: } N_U = 4$$

$$\text{From Step 7: } N_E = 4$$

so that

$$N_D = N_U - N_E = 4 - 4 = 0$$

and a unique solution exists for the problem.

Another way to calculate the number of degrees of freedom involves starting with *all* of the variables treated as unknowns (even though some of their values are known). This approach to getting N_D avoids missing one or more variables in the analysis if carried out with just the obvious variables selected as unknowns. Look at Table 7.3 in which all of the possible variables involved in the problems in Example 7.2 are listed as symbols, a total of nine.

The columns headed “Feed,” “Water,” and “Product” each correspond to a flow stream in the process, and each row corresponds to a component in the respective stream, or to the total flow. Because the example process we have been using is steady state, you do not have to take into account the variables *inside* the system. Their values are the same as those of the product stream because the internal material in the mixer is assumed to be well mixed.

TABLE 7.3 A List of All of the Variables Involved in the Example Problem

Species	Streams		
	Feed	Water	Product
NaOH	F_{NaOH}	W_{NaOH}	P_{NaOH}
H ₂ O	$F_{\text{H}_2\text{O}}$	$W_{\text{H}_2\text{O}}$	$P_{\text{H}_2\text{O}}$
Total	F	W	P

Let's analyze Example 7.2 again taking into account all of the variables. You can count the number of variables in Example 7.2 simply by multiplying the number of rows by the number of columns in the table. Let

N_{sp} = the number of species

N_{s} = the number of streams

N_{U} = the total number of variables

Then for one stream

$$N_{\text{U}} = (N_{\text{sp}} + 1) \quad \text{and for the whole process } N_{\text{U}} = 3(2 + 1) = 9$$

The value of 1 in $(N_{\text{sp}} + 1)$ comes from the last row in the table listing the totals.

What kinds of independent specifications and constraints in general must you consider in arriving at a value for N_{E} ? Here are some common possibilities:

a. *Specifications and values of variables that are given in the problem statement such as*

1. The ratio of two flow rates is some specific value.
2. The percent conversion in a reaction is given.
3. The value of a concentration, flow rate, temperature, pressure, density, volume, and so on is given.
4. A variable is not present in a stream, hence its value is zero.

For the specific case of the problem in Example 7.2 we have

- (1) Two specifications of the mass fractions and one specification of the mass flow:

$$F_{\text{NaOH}} = 1000 \text{ kg (the basis)} \quad (1)$$

$$\omega_{\text{NaOH}}^{\text{F}} = 1 \text{ or, for the variables in Table 7.3,}$$

$$\omega_{\text{H}_2\text{O}}^{\text{F}} = 0, \text{ hence } F_{\text{H}_2\text{O}} = 0 \quad (2)$$

$$\omega_{\text{H}_2\text{O}}^{\text{W}} = 1 \text{ or, for the variable in Table 7.3,}$$

$$\omega_{\text{NaOH}}^{\text{W}} = 0, \text{ hence } W_{\text{NaOH}} = 0 \quad (3)$$

(2) One specification of the ratio of two variables:

$$W/P = 0.9 \quad (4)$$

b. *Independent material balances that you can write*

For the example problem, you can write two independent material balances: one for NaOH and one for H₂O. The total balance could be substituted for either one of the two respective component balances

$$\text{NaOH balance} \quad (5)$$

$$\text{H}_2\text{O balance} \quad (6)$$

c. *Summation of the components, or the mass or mole fractions, in an individual stream*

In each stream (and inside the system) the sum of the mass or mole fractions equals unity, or, the equivalent, the sum of the mass or moles of each component in a stream equals the total material in the stream. One such equation exists for each stream flowing in and out of the system, and one for the components in each phase inside the system. In Example 7.2, three streams exist, hence three more independent equations exist.

$$\sum_i \omega_i^F = 1 \quad \text{or} \quad F_{\text{NaOH}} + F_{\text{H}_2\text{O}} = F \quad (7)$$

$$\sum_i \omega_i^W = 1 \quad \text{or} \quad W_{\text{NaOH}} + W_{\text{H}_2\text{O}} = W \quad (8)$$

$$\sum_i \omega_i^P = 1 \quad \text{or} \quad P_{\text{NaOH}} + P_{\text{H}_2\text{O}} = P \quad (9)$$

If you count all of the equations listed above for the example problem, you get a total of 9. You can then say that $N_D = N_V - N_E = 9 - 9 = 0$, where N_E is the number of independent equations. Whether you introduce some of values of the known specifications (the easy ones) into the problem prior to carrying out the degrees of freedom analysis in order to reduce the number of variables to be considered is up to you. The outcome for the degrees of freedom will be the same.

EXAMPLE 7.4 Analysis of the Degrees of Freedom

A cylinder containing CH₄, C₂H₆, and N₂ has to be prepared containing a CH₄ to C₂H₆ mole ratio of 1.5 to 1. Available to prepare the mixture are (1) a cylinder containing a mixture of 80% N₂ and 20% CH₄, (2) a cylinder containing a mixture of 90% N₂ and 10% C₂H₆, and (3) a cylinder containing pure N₂. What is the number of degrees of freedom, i.e., the number of independent specifications that

must be made, so that you can determine the respective contributions from each cylinder to get the desired composition in the cylinder with the three components?

Solution

A sketch of the process greatly helps in the analysis of the degrees of freedom. Look at Figure E7.4.

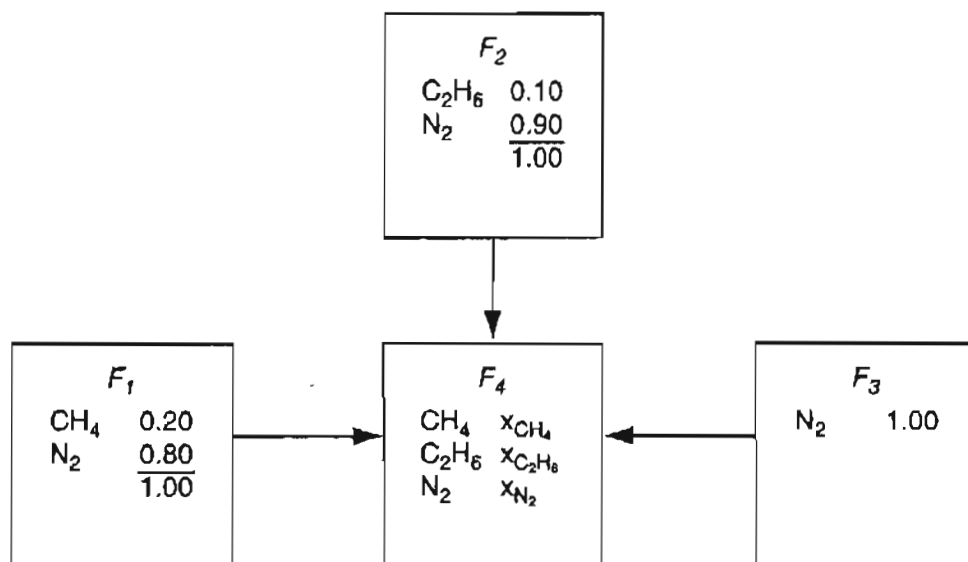


Figure E7.4

Do you count seven unknowns—three values of x_i and four values of F_i ? How many independent equations can be written?

Three material balances: CH_4 , C_2H_6 , and N_2

One specified ratio: moles of CH_4 to C_2H_6 equal 1.5 or $(x_{\text{CH}_4}/x_{\text{C}_2\text{H}_6}) = 1.5$

One summation of mole fractions: $\sum x_i^{F_4} = 1$

Thus, there are seven minus five equals two degrees of freedom. If you pick a basis, such as $F_4 = 1$, one other value has to be specified to solve the problem to calculate composition of F_4 . Keep in mind that you must be careful in making any specifications to maintain only independent equations. Avoid transforming one or more independent equations in a set such that the resulting set contains redundant (dependent) equations. Did you notice in the problem formulation that the $\sum x_i = 1$ equations for F_1 , F_2 , and F_3 were redundant because of the way the specification of the mole fractions was made?

EXAMPLE 7.5 Analysis of the Degrees of Freedom in the Production of Biomass

In the growth of biomass $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.16}\text{S}_{0.0045}\text{P}_{0.0055}$, with the system comprised of the biomass and the substrate, the substrate contains the carbon source for growth, $\text{C}_\alpha\text{H}_\beta\text{O}_\gamma$, plus NH_3 , O_2 , H_2O , CO_2 , H_3PO_4 , and H_2SO_4 . The relations between the elements and the compounds in the system (refer to Appendix L for more details) are:

	$\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.16}\text{S}_{0.0045}\text{P}_{0.0055}$	$\text{C}_\alpha\text{H}_\beta\text{O}_\gamma$	NH_3	O_2	CO_2	H_2O	H_2SO_4	H_3PO_4
C	1	α	0	0	1	0	0	0
H	1.8	β	3	0	0	2	2	3
O	0.5	γ	0	2	2	1	4	4
N	0.16	0	1	0	0	0	0	0
S	0.0045	0	0	0	0	0	1	0
P	0.0055	0	0	0	0	0	0	1

How many degrees of freedom exist for this system (assuming that the values of α , β , and γ are specified)?

Solution

Based on the given data six element balances exist for the 8 species present, hence the system has two degrees of freedom. However, it turns out for this type of system that experiments show that the change in $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.16}\text{S}_{0.0045}\text{P}_{0.0055}$ and the change in $\text{C}_\alpha\text{H}_\beta\text{O}_\gamma$ prove to be related by the amount of biomass present and the maintenance coefficient (the moles of substrate per mole of biomass per second) so that the respective quantities cannot be chosen independently. Consequently, with this extra constraint, only one degree of freedom remains to be specified, the basis.

8. Write down the equations to be solved in terms of the knowns and unknowns.

Thus [Beatrice] began: "You dull your own perceptions with false imaginings and do not grasp what would be clear but for your preconceptions."

Once you have concluded from the degree of freedom analysis that you can solve a problem, you are prepared to write down the equations to be solved (if you have not already done so as part of Step 7). Bear in mind that some formulations of the equations are easier to solve by hand, and even by using a computer, than others. In particular, you should attempt to write linear equations rather than nonlinear ones. Recall that the product of variables, or the ratios of variables, or a logarithm or exponent of a variable, and so on, in an equation causes the equation to be nonlinear.

In many instances you can easily transform a nonlinear equation to a linear one. For instance, in the problem posed in Example 7.2, one constraint given was that $W/P = 0.9$, a nonlinear equation. If you multiply both sides of the equation by P , you obtain a linear equation $W = 0.9P$.

Another example of the judicious formulation of equations occurs in the same problem. We chose as the variables listed in Table 7.3 the mass flows such as $W_{\text{H}_2\text{O}}$ and $P_{\text{H}_2\text{O}}$ for the water in the respective streams. If, instead of $P_{\text{H}_2\text{O}}$, you use as variables the product of the mass fraction of water in P times P :

$$P_{\text{H}_2\text{O}} = \omega_{\text{H}_2\text{O}}^P P$$

and substitute the product $\omega_{\text{H}_2\text{O}}^P P$ for $P_{\text{H}_2\text{O}}$ in the table and in the material balance for water, instead of having a linear equation for the water balance

$$F(0) + W(1.000) = P_{\text{H}_2\text{O}}$$

you would have

$$F(0) + W(1.000) = \omega_{\text{H}_2\text{O}}^P P$$

a nonlinear equation (which is why we didn't use $\omega_{\text{H}_2\text{O}}^P$ as a variable).

With these ideas in mind, you can formulate the set of equations to be used to solve the problem in Example 7.2 as follows. First, you introduce specifications (1), (2), and (3) into the material balances (5) and (6), and into the summation of mass fractions or their equivalents, (7), (8), and (9). Then you will obtain a set of four independent equations in four unknowns, which are the same reduced set of four unknowns we introduced at the beginning of Step 7. The basis is still 1 hr ($F_{\text{NaOH}} = 1000$ kg), and the process has been assumed to be at steady state. Recall from Chapter 6 that in such circumstances a material balance simplifies to $\text{in} = \text{out}$ or $\text{in} - \text{out} = 0$. The four equations are

$$\text{NaOH balance: } 1000 = P_{\text{NaOH}} \quad \text{or} \quad 1000 - P_{\text{NaOH}} = 0 \quad (1)$$

$$\text{H}_2\text{O balance: } W = P_{\text{H}_2\text{O}} \quad \text{or} \quad W - P_{\text{H}_2\text{O}} = 0 \quad (2)$$

$$\text{Given ratio: } W = 0.9P \quad \text{or} \quad W - 0.9P = 0 \quad (3)$$

$$\text{Sum of components in } P: P_{\text{NaOH}} + P_{\text{H}_2\text{O}} = P \quad \text{or} \quad P_{\text{NaOH}} + P_{\text{H}_2\text{O}} - P = 0 \quad (4)$$

Could you substitute the total mass balance $1000 + W = P$ for one of the two component mass balances? Of course. In fact, you could calculate P by solving just two equations:

$$\text{Total balance: } 1000 + W = P$$

$$\text{Given ratio: } W = 0.9P$$

Substitute the second equation into the first equation and solve for P .

You can conclude that the symbols you select in writing the equations and the particular equations you select to solve a problem do make a difference, and require some thought. With practice and experience in solving problems, such issues should resolve themselves.

9. Solve the equations and calculate the quantities asked for in the problem

"Problems worthy of attack prove their worth by hitting back"

Piet Hein

Industrial-scale problems may involve thousands of equations. Clearly, in such cases efficient numerical procedures for the solution of the set of equations are essential. Process simulators exist to carry out the task on a computer, as explained in Chapter 31. Because most of the problems used in this text have been selected for the purpose of communicating ideas, you will find that their solution will involve only a small set of equations. You can solve two or three equations by successive substitution. For a larger set of equations or for nonlinear equations, use a computer program such as Polymath, Excel, Matlab, or MathCad. You will save time and effort by doing so.

Learn to be efficient at problem solving.

When given data in the AE system of units, say pounds, do not first convert the data to the SI system, say kilograms, solve the problem, and then convert your results back to the AE system of units. The procedure will work, but it is quite inefficient, and introduces unnecessary opportunities for numerical errors to occur.

Select a precedence order for solving the equations you write. One choice of an order can be more effective than another. We showed in Step 8 how the choice of the total balance plus the ratio $W/P = 0.9$ led to two coupled equations that could easily be solved by substitution for W to get

$$P = 10,000 \text{ kg}$$

$$W = 9,000 \text{ kg}$$

From these two values you can calculate the amount of H_2O and NaOH in the product

$$\text{From the } \begin{cases} \text{NaOH balance:} \\ \text{H}_2\text{O balance:} \end{cases} \text{ you get } \begin{cases} P_{\text{NaOH}} = 1000 \text{ kg} \\ P_{\text{H}_2\text{O}} = 9000 \text{ kg} \end{cases}$$

Then

$$\omega_{\text{NaOH}}^P = \frac{1000 \text{ kg NaOH}}{10,000 \text{ kg Total}} = 0.1$$

$$\omega_{\text{H}_2\text{O}}^P = \frac{9,000 \text{ kg H}_2\text{O}}{10,000 \text{ kg Total}} = 0.9$$

Examine the set of four equations listed in Step 8. Can you find a shorter or easier series of calculations to get a solution for the problem?

10. Check your answer(s)

Error is a hardy plant; it flourishes in every soil.

Martin F. Tupper

Everyone makes mistakes. What distinguishes a good engineer is that he or she is able to find their mistakes before they submit their work. In Chapter 1 we listed several ways to validate your solution. We will not repeat them here. Refer to Section 1.6. A good engineer uses his or her accumulated knowledge as a primary tool to make sure that the results obtained for a problem (and the data used in the problem) are reasonable. Mass fractions should fall between zero and one. Flow rates should be nonnegative.

In any collection of data, the figure that is most obviously correct—beyond all need of checking—is the mistake.

Unknown

To the list of validation techniques that appeared in Chapter 1, we want to add one more very useful one. After solving a problem, use a redundant equation to check your values. In the problem in Example 7.2 that we have been using in the presentation of the problem-solving strategy, one of the three material balances is redundant (not independent), as pointed out several times. Supposed you had solved the problem using the NaOH and H₂O balances. Then the total balance would have been a redundant balance, and could be used to check the answers

$$P_{\text{NaOH}} + P_{\text{H}_2\text{O}} = P$$

Insert the numbers

$$1,000 + 9,000 = 10,000$$

Table 7.4 summarizes the set of 10 steps we have discussed.

If you use the steps in Table 7.4 as a mental checklist each time you start to work on a problem, you will have achieved the major objective of this chap-

TABLE 7.4 Strategy for Solving Material Balance Problems

-
1. Read and understand the problem statement.
 2. Draw a sketch of the process and specify the system boundary.
 3. Place labels for unknown variables and values for known variables on the sketch.
 4. Obtain any missing needed data.
 5. Choose a basis.
 6. Determine the number of unknowns.
 7. Determine the number of independent equations, and carry out a degree of freedom analysis.
 8. Write down the equations to be solved.
 9. Solve the equations and calculate the quantities asked for.
 10. Check your answer(s).
-

ter and substantially added to your professional skills. These steps do not have to be carried out in the order listed in the table, and you may repeat steps as the formulation of the solution of the problem becomes clearer. But each of the steps is essential even if carried out implicitly.

Postscript

Tables 7.5 and 7.6 comprise a list of traits to review to help you improve your problem-solving abilities. Also look on the CD that accompanies this book. It contains a section with a more detailed discussion of how to solve problems.

TABLE 7.5 Techniques Used by Experts to Overcome Barriers to Problem Solving

-
- Read the problem over several times, but at different times. Be sure to understand all facets of it.
 - Emphasize the different features each time.
 - Restate the problem in your own words. List assumptions.
 - Draw a comprehensive diagram of the process and enter *all* known information on the diagram. Enter symbols for unknown variables and parameters.
 - Formally write down what you are going to solve for: "I want to calculate . . ."
 - Choose a basis.
 - Relate the problem to similar problems you have encountered before, but note any differences.
 - Plan a strategy for a solution, writing it down if necessary. Consider different strategies.
 - Write down all the equations and rules that might apply to the problem.
 - Formally write down everything you know about the problem and what you believe is needed to execute a solution.
 - Talk to yourself as you proceed to solve the problem.
 - Ask yourself questions as you go along concerning the data, procedures, equations involved, etc.

TABLE 7.5 *Continued*

Talk to other people about the problem.
Break off problem solving for a few minutes and carry out some other activity.
Break up the solution of the problem into more manageable parts, and start at a familiar stage. Write down the objective for each subproblem (i.e., convert mole fraction to mass fraction, find the pressure in tank 2, etc.).
Repeat the calculations but in a different order.
Work both forward and backward in the solution scheme.
Consider if the results you obtained are reasonable. Check both units and order of magnitude of the calculations. Are the boundary conditions satisfied?
Use alternative paths to verify your solution.
Maintain a positive attitude—you know the problem can be solved, just how is the question.

TABLE 7.6 A Comparison of the Problem-Solving Habits of a Novice and an Expert

A novice:	An expert:
Starts solving a problem before fully understanding what is wanted and/or what a good route for solution will be.	Reviews the entire plan, mentally explores alternative strategies, and clearly understands what result is to be obtained.
Focuses only on a known problem set that he or she has seen before and tries to match the problem with one in the set.	Concentrates on similarities to and differences from known problems; uses generic principles rather than problem matching.
Chooses one procedure without exploring alternatives.	Examines several procedures serially or in parallel.
Emphasizes speed of solution, unaware of blunders.	Emphasizes care and accuracy in the solution.
Does not follow an organized plan of attack; jumps about and mixes problem-solving strategies.	Goes through the problem-solving process step by step, checking, reevaluating, and recycling from dead ends to another valid path.
Is unaware of missing data, concepts, laws.	Knows what principles might be involved and where to get missing data.
Exhibits bad judgment, makes unsound assumptions	Carefully evaluates the necessary assumptions.
Gives up solving the problem because he or she does not have skills to branch away from a dead-end strategy.	Aware that a dead end may exist for a strategy and has planned alternative strategies if a dead end is reached.
Unable to make approximations or makes bad ones.	Makes appropriate approximations.
Cannot conceive of disagreeing.	Disagrees with other experts.
Slavishly follows instructions; proceeds "by the book."	Breaks rules and makes exceptions.
Does not know what to make of qualitative data.	Able to deal with qualitative data.
Fritters time away.	Good management of time.

SELF ASSESSMENT TEST

Questions

1. What does the concept "solution of a material balance problem" mean?
2. (a) How many values of unknown variables can you compute from one independent material balance?
(b) From three independent material balance equations?
(c) From four material balances, three of which are independent?
3. What does the concept of independent equations mean?
4. If you want to solve a set of independent equations that contain fewer unknown variables than equations (the overspecified problem), how should you proceed with the solution?
5. What is the major category of implicit constraints (equations) you encounter in material balance problems?
6. If you want to solve a set of independent equations that contain more unknown variables than equations (the underspecified problem), what must you do to proceed with the solution?
7. As I was going to St. Ives,
I met a man with seven wives:
Every wife had seven sacks,
Every sack had seven cats,
Every cat had seven kits.
Kits, cats, sacks, and wives,
How many were going to St. Ives?

Problems

1. A water solution containing 10% acetic acid is added to a water solution containing 30% acetic acid flowing at the rate of 20 kg/min. The product P of the combination leaves at the rate of 100 kg/min. What is the composition of P ? For this process,
 - a. Determine how many independent balances can be written.
 - b. List the names of the balances.
 - c. Determine how many unknown variables can be solved for.
 - d. List their names and symbols.
 - e. Determine the composition of P .
2. Can you solve these three material balances for F , D , and P ? Explain why not.

$$0.1F + 0.3D = 0.2P$$

$$0.9F + 0.7D = 0.8P$$

$$F + D = P$$

3. How many values of the concentrations and flow rates in the process shown in Figure SAT7.2P3 are unknown? List them. The streams contain two components, 1 and 2.

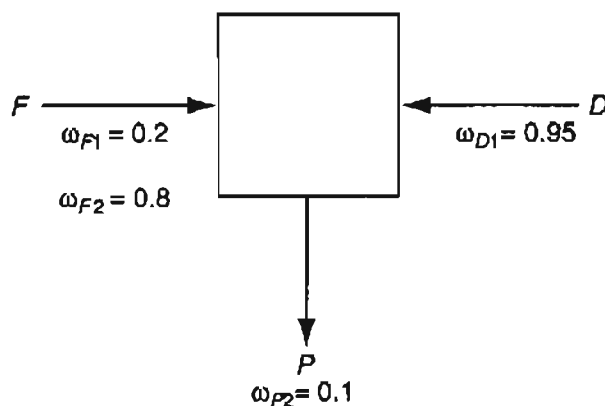


Figure SAT7.2P3

4. How many material balances are needed to solve Problem 3? Is the number the same as the number of unknown variables? Explain.

Thought Problem

1. In the steady-state flow process shown in Figure TP7.2P1, a number of values of ω (mass fraction) are not given. Mary says that nevertheless the problem has a unique solution for the unknown values of ω . Kelly says that four values of ω are missing, that you can write three component material balances, and that you can use three relations for $\sum \omega_i = 1$, one for each stream, a total of six equations, so that a unique solution is not possible. Who is right?

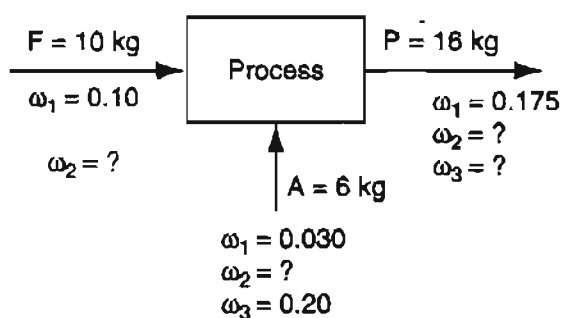


Figure TP7.2P1

Discussion Problems

1. Consider the concept of zero discharge of liquid waste. It would seem to be a good idea both for the environment and the company. What are some of the arguments for and against the zero discharge of wastewater?
2. One proposed method of eliminating waste in solid, liquid, and gas streams is incineration. What are some of the pros and cons regarding disposal of waste by incineration?

Looking Back

In this chapter we discussed a set of 10 steps that you should apply in solving material balance problems. Not all steps have to be formally written down, but each merits consideration if you want to solve problems efficiently and effectively. We recommend that you use them throughout the remainder of the book and thereafter in your practice of engineering.

GLOSSARY OF NEW WORDS

Degrees of freedom The number of variables whose values are unknown minus the number of independent equations.

Degree of freedom analysis Determination of the number of degrees of freedom in a problem.

Dependent equations A set of equations that are not independent.

Exactly specified A problem in which the number of degrees of freedom is zero.

Implicit equation An equation based on information not explicitly provided in a problem such as the sum of the mass fractions is one.

Independent equations A set of equations for which the rank of the coefficient matrix formed from the equations is the same as the number of equations.

Knowns Variables whose values are known.

Overspecified A set of equations (or a problem) that is comprised of more equations than unknowns.

Underspecified A set of equations (or a problem) that is comprised of fewer equations than unknowns.

Unique solution A single solution exists for a set of equations (or a problem).

Unknowns Variables whose values are unknown.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are also pertinent.

Felder, R. M. "The Generic Quiz," *Chem. Eng. Educ.*, 176–181 (Fall 1985).

Fogler, H. S., and S. M. Montgomery. *Interactive Computer Modules for Chemical Engineering Instruction*, CACHE Corp., Austin, TX (2000).

Woods, D. R., T. Kourti, P. E. Wood, H. Sheardown, C. M. Crowe, and J. M. Dickson. "Assessing Problem Solving Skills," *Chem. Eng. Educ.*, 300–307 (Fall 2001).

Web Site

<http://169.237.64.14/webMathematica/MSP/Examples/DOFAnalysis>

PROBLEMS

- *7.1** For the process shown in Figure P7.1, how many material balance equations can be written? Write them. How many independent material balance equations are there in the set?

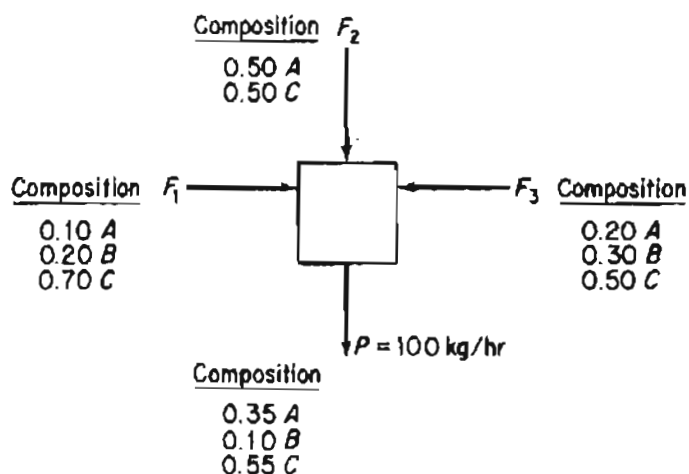


Figure P7.1

- *7.2** Examine the process in Figure P7.2. No chemical reaction takes place, and x stands for mole fraction. How many variables are unknown? How many are concentrations? Can this problem be solved uniquely for the unknowns?

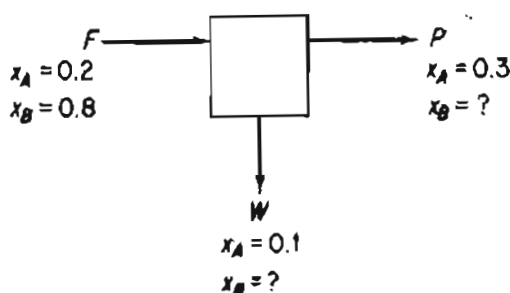


Figure P7.2

***7.3** Are the following equations independent? Do they have a unique solution? Explain your answers.

(a) $x_1 + 2x_2 = 1$

(b) $(x_1 - 1)^2 + (x_2 - 1)^2 = 0$

$x_1 + 2x_2 = 3$

$x_1 + x_2 = 1$

***7.4** For one process your assistant has prepared four valid material balances

$$0.25 m_{\text{NaCl}} + 0.35 m_{\text{KCl}} + 0.55 m_{\text{H}_2\text{O}} = 0.30$$

$$0.35 m_{\text{NaCl}} + 0.20 m_{\text{KCl}} + 0.40 m_{\text{H}_2\text{O}} = 0.30$$

$$0.40 m_{\text{NaCl}} + 0.45 m_{\text{KCl}} + 0.05 m_{\text{H}_2\text{O}} = 0.40$$

$$1.00 m_{\text{NaCl}} + 1.00 m_{\text{KCl}} + 1.00 m_{\text{H}_2\text{O}} = 1.00$$

He says that since the four equations exceed the number of unknowns, three, no solution exists. Is he correct? Explain briefly whether it is possible to achieve a unique solution.

****7.5** Do the following sets of equations have a unique solution?

$u + v + w = 0$

$u + w = 0$

(a) $u + 2v + 3w = 0$

(b) $5u + 4v + 9w = 0$

$3u + 5v + 7w = 1$

$2u + 4v + 6w = 0$

****7.6** Answer the following questions true or false:

(a) When the flow rate of one stream is given in a problem, you must choose it as the basis.

(b) If all of the stream compositions are given in a problem, but none of the flow rates are specified, you cannot choose one of the flow rates as the basis.

(c) The maximum number of material balance equations that can be written for a problem is equal to the number of species in the problem.

****7.7** In the steady state process (with no reactions occurring) in Figure P7.7 you are asked to determine if a unique solution exists for the values of the variables. Does it? Show all calculations.

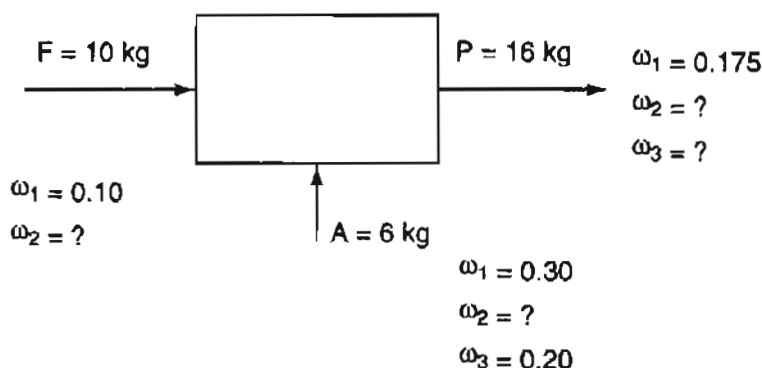


Figure P7.7

ω is the mass fraction of component i .

- *7.8** Three gaseous mixtures, A, B, and C, with the compositions listed in the table are blended into a single mixture.

Gas	A	B	C
CH ₄	25	25	60
C ₂ H ₆	35	30	25
C ₃ H ₈	40	45	15
Total	100	100	100

A new analyst reports that the composition of the mixture is 25% CH₄, 25% C₂H₆, and 50% C₃H₈. Without making any detailed calculations, explain how you know the analysis is incorrect.

- **7.9** A problem is posed as follows. It is desired to mix three LPG (Liquefied Petroleum Gas) streams denoted by A, B, and C, in certain proportions so that the final mixture will meet certain vapor pressure specifications. These specifications will be met by a stream of composition D as indicated below. Calculate the proportions in which streams A, B, and C must be mixed to give a product with a composition of D. The values are liquid volume %, but the volumes are additive for these compounds.

Component	Stream A	B	C	D
C ₂	5.0			1.4
C ₃	90.0	10.0		31.2
iso-C ₄	5.0	85.0	8.0	53.4
n-C ₄		5.0	80.0	12.6
iso-C ₅ ⁺			12.0	1.4
	100.0	100.0	100.0	100.0

The subscripts on the C's represent the number of carbons, and the + sign on C₅⁺ indicates all compounds of higher molecular weight as well as iso-C₅.

Does this problem have a unique solution?

- **7.10** In preparing 2.50 moles of a mixture of three gases, SO_2 , H_2S , and CS_2 , gases from three tanks are combined into a fourth tank. The tanks have the following compositions (mole fractions):

Gas	Tanks			Combined Mixture
	1	2	3	4
SO_2	0.23	0.20	0.54	0.25
H_2S	0.36	0.33	0.27	0.23
CS_2	0.41	0.47	0.19	0.52

In the right-hand column is listed the supposed composition obtained by analysis of the mixture. Does the set of three mole balances for the three compounds have a solution for the number of moles taken from each of the three tanks and used to make up the mixture? If so, what does the solution mean?

- **7.11** You have been asked to check out the process shown in Figure P7.11. What will be the minimum number of measurements to make in order to compute the value of each of the stream flow rates and stream concentrations? Explain your answer.

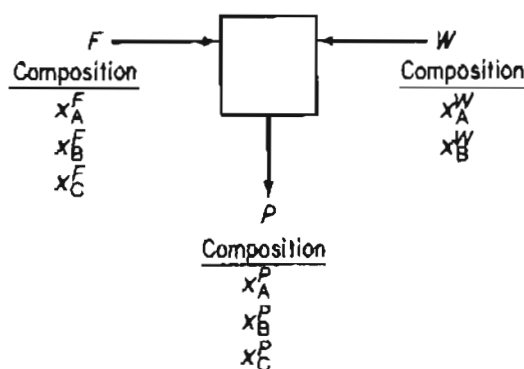


Figure P7.11

Can any arbitrary set be used; that is, can you measure just the three flow rates and two concentrations? Can you measure just three concentrations in stream F and two concentrations in stream W? No chemical reaction takes place and x is the mole fraction of component A, B, or C.

- **7.12** Effluent from a fertilizer plant is processed by the system shown in Figure P7.12. How many additional concentration and stream flow measurements must be made to completely specify the problem (so that a unique solution exists)? Does only one unique set of specifications exist?

For each of the following three problems

- Draw a figure
- Put the data in the problem on the figure

- (c) Pick a basis
- (d) Determine the number of unknowns and independent equations
- (e) Write the material balances needed to solve the problem
- (f) Write down any other pertinent equations and specifications
- (g) Solve the problem if possible

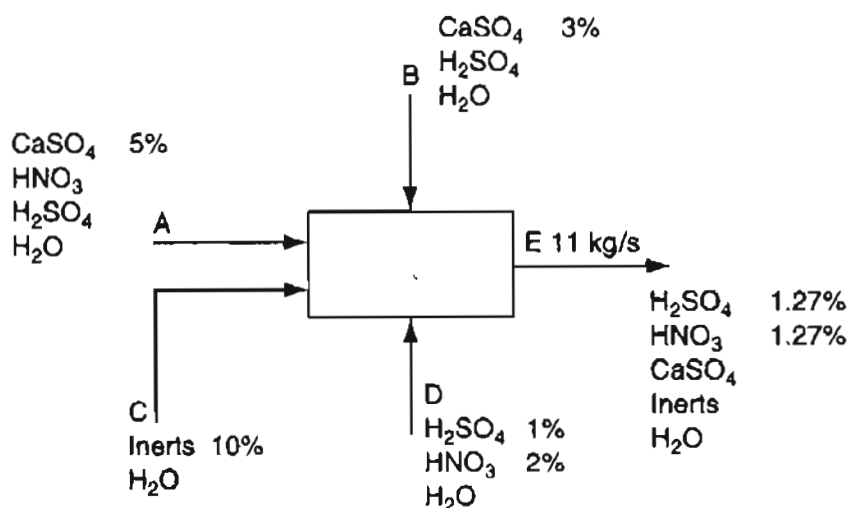


Figure P7.12

- ✓**7.13 Tank A containing 90% nitrogen is mixed with Tank B containing 30% nitrogen to get Tank C containing 65% nitrogen. You are asked to determine the ratio of the gas used from Tank A to that used from Tank B.
- **7.14 A drier takes in wet timber (20.1% water) and reduces the water content to 8.6%. You want to determine the kg of water removed per kg of timber that enters the process.
- ✓**7.15 A cylinder containing CH₄, C₂H₆, and N₂ has to be prepared in which the ratio of the moles of CH₄ to C₂H₆ is 1.3 to 1. Available are (1) a cylinder containing a mixture of 70% N₂ and 30% CH₄, (2) a cylinder containing a mixture of 90% N₂ and 10% C₂H₆, and a cylinder of pure N₂. Determine the proportions in which the respective gases from each cylinder should be used.
- *7.16 After you read a problem statement, what are some of the things you should think about to solve it. List them. This problem does not ask for the 10 stages described in the chapter, but for brain storming.

CHAPTER 8

SOLVING MATERIAL BALANCE PROBLEMS FOR SINGLE UNITS WITHOUT REACTION

Your objectives in studying this chapter are to be able to:

1. Analyze a problem statement and organize in your mind the solution strategy.
2. Apply the 10-step strategy to solve problems without chemical reactions.

In Chapters 6 and 7 you read about solving material balance problems without reaction. Can you apply these ideas now? If you are quite confident, you might go on to the next chapter. If not, hone your skills by going through the applications presented in this chapter.

Looking Ahead

In this chapter we are going to go through several examples that involve the analysis and solution of material balances for a single system. If you hope to develop some skill and judgment in solving material balance problems, the way to proceed through this chapter is to first cover up the solution of the problem, then read the problem, then sketch out on a piece of paper your solution step by step, and only afterward look at the solution that appears in the example. If you just read the problem and its solution, you will deprive yourself of the learning activity needed to improve your capabilities. You will find additional solved problems on the CD that ac-

companies this book if you would like more practice in developing your problem-solving skills.

Main Concepts

A famous magician stood on a concrete floor, and with a flourish pulled a raw egg from his hair. He held the egg in his outstretched hand, and said he could drop it 2 meters without breaking its shell and without the aid of any other object. Then he proceeded to do it. What did he do? (The answer is at the end of the chapter.)

Problem solving is what you do when you don't know what to do; otherwise it's not a problem.

G. Bodner, *J. Chem. Edu.* **63**, 873 (1986)

The use of material balances in a process allows you (a) to calculate the values of the total flows and flows of species in the streams that enter and leave the plant equipment, and (b) to calculate the change of conditions inside the equipment. You want to find out how much of each raw material is used and how much of each product (along with some wastes) is obtained from the plant. We use simple examples in this chapter to demonstrate that no matter what the process is, the problem-solving strategy evolved in Chapter 7 can be effective for all of them. If the process involves rates of flow, you can pick an interval of time as the basis on which to solve the problem so that you can avoid carrying along time as a symbol or variable in the analysis and calculations.

EXAMPLE 8.1 Extraction of Streptomycin from a Fermentation Broth

Streptomycin is used as an antibiotic to fight bacterial diseases, and is produced by the fermentation of a bacterium in a biological reactor with a nutrient of glucose and amino acids. After the fermentation process, Streptomycin is recovered by contacting the fermentation broth with an organic solvent in an extraction process. The extraction process is able to recover the Streptomycin because Streptomycin has a greater affinity for dissolving in the organic solution than in the aqueous solution. Figure E8.1 shows the overall process.

Determine the mass fraction of Streptomycin in the exit organic solvent assuming that no water exits with the solvent and no solvent exits with the aqueous solution. Assume that the density of the aqueous solution is 1 g/cm^3 and the density of the organic solvent is 0.6 g/cm^3 .

Solution**Step 1**

This is an open (flow), steady-state process without reaction. Assume because of the low concentration of Strep. in the aqueous and organic fluids that the flow rates of the entering fluids equal the flow rates of the exit fluids.

Steps 2, 3, and 4

All of the data has been placed on Figure E8.1.

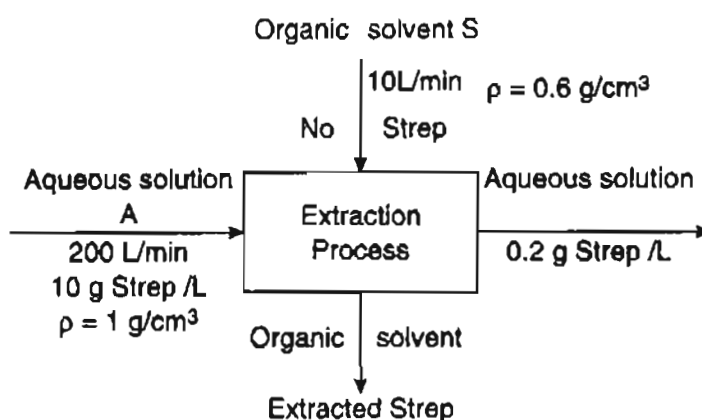


Figure E8.1

Step 5

Basis: 1 min

Steps 6 and 7

The degree-of-freedom analysis is:

Number of variables (8): 4 flows (in L) plus 4 concentrations (in g/L)

Number of equations (8):

Basis: Feed = 200 L (flow of aqueous entering aqueous solution)	1
Specifications: Concentration of Strep in entering aqueous solution	1
Concentration of Strep in exit aqueous solution	1
Concentration of Strep in entering organic solvent	1
Flow of exiting aqueous solution (same as existing flow)	1
Flow of entering organic solution	1
Flow of exiting organic solution (same as existing flow)	1
Strep material balance	<u>1</u>
Total	8

The degrees of freedom are 0.

Steps 8 and 9

The material balances are *in = out* in grams. Let x be the g of Strep per L of solvent S.

Strep. balance:

$$\frac{200 \text{ L of A}}{1 \text{ L of A}} \left| \frac{10 \text{ g Strep}}{1 \text{ L of A}} \right| + \frac{10 \text{ L of S}}{1 \text{ L of S}} \left| \frac{0 \text{ g Strep}}{1 \text{ L of S}} \right| = \frac{200 \text{ L of A}}{1 \text{ L of A}} \left| \frac{0.2 \text{ g Strep}}{1 \text{ L of A}} \right| + \frac{10 \text{ L of S}}{1 \text{ L of S}} \left| \frac{x \text{ g Strep}}{1 \text{ L of S}} \right|$$

$$x = 196 \text{ g Strep/L of S}$$

To get the g Strep/g solvent, use the density of the solvent:

$$\frac{196 \text{ g Strep}}{1 \text{ L of S}} \left| \frac{1 \text{ L of S}}{1000 \text{ cm}^3 \text{ of S}} \right| \left| \frac{1 \text{ cm}^3 \text{ of S}}{0.6 \text{ g of S}} \right| = 0.3267 \text{ g Strep/g of S}$$

$$\text{The mass fraction Strep} = \frac{0.3267}{1 + 0.3267} = 0.246$$

EXAMPLE 8.2 Separation of Gases Using a Membrane

Membranes represent a relatively new technology for the separation of gases. One use that has attracted attention is the separation of nitrogen and oxygen from air. Figure E8.2a illustrates a nanoporous membrane that is made by coating a very thin layer of polymer on a porous graphite supporting layer.

What is the composition of the waste stream if the waste stream amounts to 80% of the input stream?

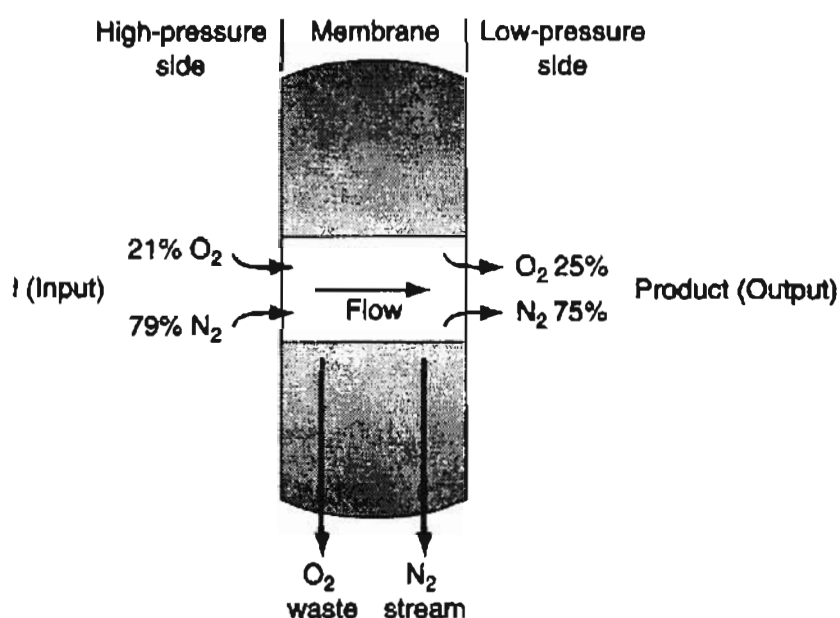
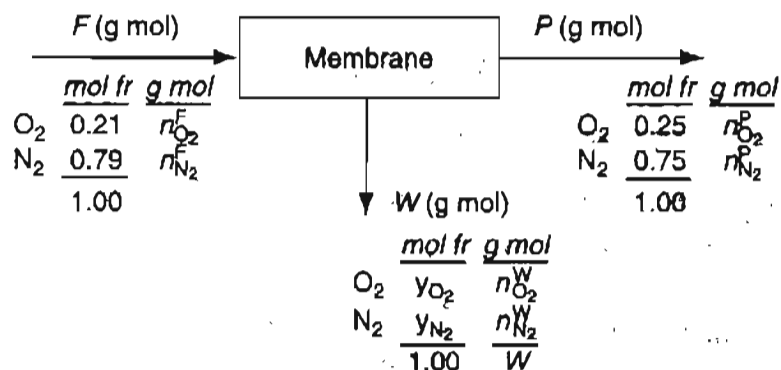


Figure E8.2a

Solution**Step 1**

This is an open, steady-state process without chemical reaction. The system is the membrane as depicted in Figure E8.2. Let y_{O_2} be the mole fraction of oxygen as depicted in Figure E8.2, y_{N_2} be the mole fraction of nitrogen, and let n_{O_2} and n_{N_2} be the respective moles.

**Figure E8.2b****Steps 2, 3, and 4**

All of the data and symbols have been placed in Figure E8.2b.

Step 5 Pick a convenient basis.

Basis: 100 g mol = F

A degree of freedom analysis that includes all of the variables comes next. You could either use moles or mole fractions as the unknowns.

Steps 6 and 7

Number of variables: 9

F , P , W and 6 n_i

Number of equations: 9

Basis: $F = 100$

Specifications: $n_{O_2}^F = 0.21(100) = 21$

$n_{N_2}^F = 0.79(100) = 79$

$y_{O_2}^P = n_{O_2}^P/P = 0.25$ $n_{O_2}^P = 0.25P$

$y_{N_2}^P = n_{N_2}^P/P = 0.75$ $n_{N_2}^P = 0.75P$

$W = 0.80(100) = 80$

Material balances: O_2 and N_2

Implicit equations: $\sum n_i^W = W$ or $\sum y_i^W = 1$

The problem has zero degrees of freedom because of the way we have formulated the solution. Note that $n_{O_2}^F + n_{N_2}^F = F$ is a redundant equation because it repeats some of the specifications. Also, $n_{O_2}^P + n_{N_2}^P = P$ is redundant. Divide the equation by P to get $y_{O_2}^P + y_{N_2}^P = 1$, a relation that is equivalent to the sum of two of the specifications.

Step 8

If you introduce the known values into the species balances and implicit equation, you get three independent equations in three unknowns

	<u>In</u>	<u>Out</u>		<u>In</u>	<u>Out</u>
O_2 :	0.21 (100)	$= 0.25P + y_{O_2}^W (80)$	or	0.21 (100)	$= 0.25P + n_{O_2}^W$
N_2 :	0.79 (100)	$= 0.75P + y_{N_2}^W (80)$	or	0.79 (100)	$= 0.75P + n_{N_2}^W$
	1.00	$= y_{O_2}^W + y_{N_2}^W$	or	80	$= n_{O_2}^W + n_{N_2}^W$

Step 9

The solution of these equations is $n_{O_2}^W = 16$ and $n_{N_2}^W = 64$, or $y_{O_2}^W = 0.20$ and $y_{N_2}^W = 0.80$, and $P = 20$ g mol.

An alternate calculation involves the use of the total balance first in place of one component balance. The overall balance is easy to solve because

$$F = P + W \text{ or } 100 = P + 80$$

gives $P = 20$ straight off. Then, the oxygen balance would be

$$0.21(100) = 0.25(20) + n_{O_2}^W$$

from which you can get $n_{O_2}^W = 16$ g mol, and $n_{N_2}^W = 80 - 16 = 64$ g mol. Alternately, you could use the nitrogen balance to get the same result.

Step 10

Check. You can use the total balance as a check on the solution obtained from the two component balances

$$100 = 20 + 80 \text{ OK}$$

Be careful in formulating and simplifying the equations to be solved to make sure that the set evolves into a *set of independent equations*. For example, if you prepare the following set of equations from the data given in a problem with zero degrees of freedom,

$$0.25m_{\text{NaCl}} + 0.35m_{\text{KCl}} + 0.55m_{\text{H}_2\text{O}} = 0.30$$

$$0.35m_{\text{NaCl}} + 0.20m_{\text{KCl}} + 0.40m_{\text{H}_2\text{O}} = 0.30$$

$$0.40m_{\text{NaCl}} + 0.45m_{\text{KCl}} + 0.05m_{\text{H}_2\text{O}} = 0.40$$

$$1.00m_{\text{NaCl}} + 1.00m_{\text{KCl}} + 1.00m_{\text{H}_2\text{O}} = 1.00$$

it may appear that the set contains three unknowns and four equations. However, only three of the equations are independent. Do you see why?

In the next problem we give an example of distillation. Distillation is the most commonly used process for separating components, and is based on the separation that results from vaporizing a liquid (see Chapter 16). When a liquid mixture is boiled to produce a vapor, the vapor contains a higher concentration of the more volatile component. A distillation column is a collection of a number of stages that lead to the concentration of the more volatile components in the top product from the column and the concentration of the less volatile components in the bottom product of the column. Look on the CD accompanying this book for more information about the specialized terminology pertaining to distillation and pictures of distillation equipment.

EXAMPLE 8.3 Overall Analysis for a Continuous Distillation Column

A novice manufacturer of ethyl alcohol (denoted as EtOH) for gasohol is having a bit of difficulty with a distillation column. The process is shown in Figure E8.3. It appears that too much alcohol is lost in the bottoms (waste). Calculate the composition of the bottoms and the mass of the alcohol lost in the bottoms based on the data shown in Figure E8.3 that was collected during 1 hour of operation.

Solution

Although the distillation unit shown in Figure E8.3 is comprised of more than one unit of equipment, you can select a system that includes all of the equipment inside the system boundary. Consequently, you can ignore all the internal streams for

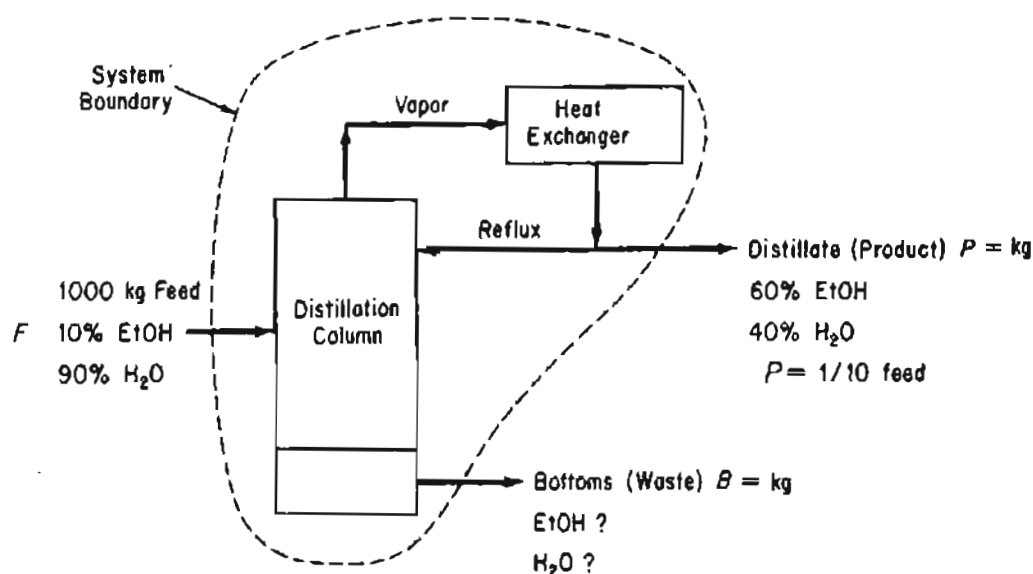


Figure E8.3

this problem. Let m designate the mass of a component. Clearly the process is an open system, and we assume it is in the steady state. No reaction occurs. Thus, the material balances reduce to $In = Out$ in kg. The cooling water enters and leaves the heat exchanger without mixing with the components being separated, and can be ignored for the material balances. In addition, the heat added at the bottom of the column does not involve mass entering or leaving the system, and can be ignored for the material balances.

Steps 1, 2, 3, and 4

All of the symbols and known data have been placed on Figure E8.3.

Step 5

Select as the basis the given feed. Pick 1 hour so that you can suppress the time variable in all of the calculations.

Basis: 1 hour so that $F = 1000$ kg of feed

Step 4

We are given that P is $\frac{1}{10}$ of F , so that $P = 0.1(1000) = 100$ kg

Steps 6 and 7

The next step is to carry out a degree of freedom analysis.

Number of variables: 9

$$m_{\text{EtOH}}^F, m_{\text{H}_2\text{O}}^F, m_{\text{EtOH}}^P, m_{\text{H}_2\text{O}}^P, m_{\text{EtOH}}^B, m_{\text{H}_2\text{O}}^B, F, P, B$$

Number of equations: 9

Basis: $F = 1000$ kg

Specifications: $m_{\text{EtOH}}^F = 1000(0.10) = 100$

$$m_{\text{H}_2\text{O}}^F = 1000(0.90) = 900$$

$$m_{\text{EtOH}}^P = 0.60P$$

$$m_{\text{H}_2\text{O}}^P = 0.40P$$

$$P = 0.1 F = 100 \text{ kg}$$

Material balances: EtOH and H₂O

Implicit equations: $\sum m_i^B = B$ or $\sum \omega_i^B = 1$

The problem has zero degrees of freedom. What redundant equation(s) can you write? Refer back to Example 8.2 for hints.

Steps 8 and 9

Let's substitute the total mass balance $F = P + B$ for one of the component mass balances and calculate B by direct subtraction

$$B = 1000 - 100 = 900 \text{ kg}$$

The solution for the composition of the bottoms can then be computed directly from the material balances:

	<i>kg feed in</i>	<i>kg distillate out</i>	<i>kg bottoms out</i>	<i>Mass fraction</i>
EtOH balance:	$0.10(1000)$	$- 0.60(100)$	$= 40$	0.044
H ₂ O balance:	$0.90(1000)$	$- 0.40(100)$	$= \underline{860}$	<u>0.956</u>
			900	1.000

Step 10 As a check let's use the redundant equation

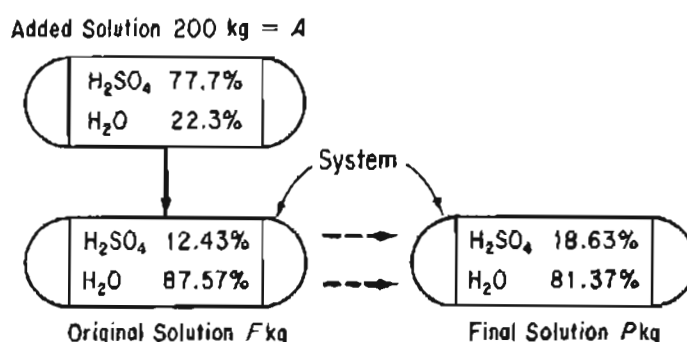
$$m_{\text{EtOH}}^B + m_{\text{H}_2\text{O}}^B = B \quad \text{or} \quad \omega_{\text{EtOH}}^B + \omega_{\text{H}_2\text{O}}^B = 1$$

Examine the last two columns of the table above for verification.

The next example represents an open system, but one that is in the unsteady state. The CD that accompanies this book shows various equipment used to mix liquids.

EXAMPLE 8.4 Mixing of Battery (Sulfuric) Acid

You are asked to prepare a batch of 18.63% battery acid as follows. A tank of old weak battery acid (H_2SO_4) solution contains 12.43% H_2SO_4 (the remainder is pure water). If 200 kg of 77.7% H_2SO_4 is added to the tank, and the final solution is to be 18.63% H_2SO_4 , how many kilograms of battery acid have been made? See Figure E8.4.

**Figure E8.4****Solution****Steps 1, 2, 3, and 4.**

All of the values of the compositions are known and have been placed on Figure E8.4. No reaction occurs. Should the process be treated as an unsteady-state process or a steady-state process? If the tank is selected as the system, and the tank initially contains sulfuric acid solution, then a change occurs inside the system so that accumulation occurs in the system: the total mass increases and the mass of each component increases

$$\text{accumulation} = \text{in} - \text{out}$$

From another viewpoint, as you learned in Chapter 7, you could regard the tank as initially being empty, the original solution is introduced into the system along with the 200 kg of 77.7% solution, the solutions are mixed, and finally the entire contents of the tank are removed leaving an empty tank. Then, the mass balance reduces to a steady-state flow process

$$\text{in} = \text{out}$$

because no accumulation occurs in the tank.

Let us first solve the problem with the mixing treated as an unsteady-state process, and then repeat the solution with the mixing treated as a steady-state process.

Step 5. Take 200 kg of A as the basis for convenience.

Step 6 and 7

The degree-of-freedom analysis is analogous to the ones carried out for Examples 8.2 and 8.3.

Number of variables: 9

$$m_{\text{H}_2\text{SO}_4}^A, m_{\text{H}_2\text{O}}^A, m_{\text{H}_2\text{SO}_4}^F, m_{\text{H}_2\text{O}}^F, m_{\text{H}_2\text{SO}_4}^P, m_{\text{H}_2\text{O}}^P, A, F, P$$

Number of equations: 9

Basis: $A = 200$ kg

Specifications:

$$\omega_{\text{H}_2\text{SO}_4}^A, \omega_{\text{H}_2\text{O}}^A, \omega_{\text{H}_2\text{SO}_4}^F, \omega_{\text{H}_2\text{O}}^F, \omega_{\text{H}_2\text{SO}_4}^P, \omega_{\text{H}_2\text{O}}^P$$

Material balances

H_2SO_4 and H_2O

The degrees of freedom are zero. Note that the implicit equations $\sum \omega_i = 1$ for A , F , and P are redundant because of the specifications of the mass fractions. Is $P = A + F$ redundant also?

Step 8

We will insert the basis and specifications into the mass balances. The balances will be in kilograms.

Type of Balance	Accumulation in Tank				In		Out
	Final	Initial					
H_2SO_4	$P(0.1863)$	$-$	$F(0.1243)$	$=$	$200(0.777)$	$-$	0
H_2O	$P(0.8137)$	$-$	$F(0.8757)$	$=$	$200(0.223)$	$-$	0
Total	P	$-$	F	$=$	200	$-$	0

Note that any pair of the three equations is independent.

Step 9

Because the equations are linear and only two independent equations occur, you can take the total mass balance, solve it for F , and substitute for F in the H_2SO_4 balance to calculate P and get

Figure E8.5

cake), 100 kg of water is removed, and it is found that the fish cake is then 40% water. Calculate the weight of the fish cake originally put into the dryer. Figure E8.5 is a diagram of the process.

Solution

We will abbreviate the solution.

Steps 1, 2, 3, and 4

This is a steady-state process without reaction. The system is the dryer.

Step 5

Take a basis of what is given.

Basis: 100 kg of water evaporated = W

Steps 6 and 7

The degree-of-freedom analysis gives zero degrees of freedom. There are four streams, two in (air and fish cake) and two out (air and fish cake), although the air is not shown in Figure E8.5 because it is not involved in the process. Only the water in the air is involved. Two independent balances can be written. We will use the total mass balance plus the BDC (bone dry cake) balance (the tie component) in kg.

The water balance

$$0.80A = 0.40B + 100$$

can be used as a check on the calculations.

	<i>In</i>	<i>Out</i>	
Total balance:	A	$= B + W = B + 100$	}
BDC balance:	$0.20A$	$= 0.60B$	

mass balances

The solution is

$$A = 150 \text{ kg initial cake and } B = (150)(0.20/0.60) = 50 \text{ kg}$$

Step 10

Check via the water balance:

$$0.80(150) \stackrel{?}{=} 0.40(50) + 100$$

$$120 = 120$$

In Example 8.5 the BDC in the wet and dry fish cake is known as a **tie component** because the BDC goes from a single stream in the process to another single stream without loss, addition, or splitting. The BDC ties two streams together. Consequently, if you pick BDC as the basis in the problem, you can add and subtract ratios of the amount of a compound per unit amount of BDC in a material balance. Here is what you could have done in Example 8.5:

Basis: 1 kg BDC

H₂O balance:

$$\begin{array}{rcccl} & \text{In} & & \text{Out} & \\ \hline & 0.80 \text{ kg H}_2\text{O in A} & & 0.40 \text{ kg H}_2\text{O in B} & \\ \hline & 0.20 \text{ kg BDC in A} & - & 0.60 \text{ kg BDC in B} & = \end{array} \quad \begin{array}{c} \text{H}_2\text{O removed} \\ \hline 3.33 \text{ kg H}_2\text{O} \\ \hline \text{kg BDC (in A or B)} \end{array}$$

Next, shift to a basis of 100 kg of H₂O in W. The H₂O removed is H₂O in W:

$$\begin{array}{c|c|c} 100 \text{ kg H}_2\text{O in W} & 1 \text{ kg BDC in A} & 1.00 \text{ kg A} \\ \hline & 3.33 \text{ kg H}_2\text{O removed} & 0.20 \text{ kg BDC in A} \\ \hline \end{array} = 150 \text{ kg A}$$

Sometimes the use of a tie element reduces the extent of the calculations in a problem.

EXAMPLE 8.6 Crystallization

A tank holds 10,000 kg of a saturated solution of Na₂CO₃ at 30°C. You want to crystallize from this solution 3000 kg of Na₂CO₃ · 10H₂O without any accompanying water. To what temperature must the solution be cooled?

Solution

This problem is a little more complicated to analyze than the previous problems because it not only requires a decision as to what the compounds are in the problem, but also it implies without specifically stating so that the *final solution is saturated at the final temperature*. No reaction occurs. Although the problem could be set up as a steady-state problem with flows in and out of the system (the tank), it is equally justified to treat the process as an unsteady-state process. The major difficulty posed in this problem is to get all the necessary information about the compositions of the solutions and solid precipitate. If you can calculate the final concentration of the Na₂CO₃ in the tank, you can look up the corresponding temperature in a handbook containing solubility data. The components mentioned in the problem statement are Na₂CO₃, H₂O, and Na₂CO₃ · 10H₂O. Although these components can

exist as separate compounds, only two chemical species actually exist in the tank: Na_2CO_3 and H_2O . Let's select these species as the components for which to make material balances, because it takes fewer steps to make the required calculations.

Steps 1, 2, and 3

Figure E8.6a is a diagram of the process

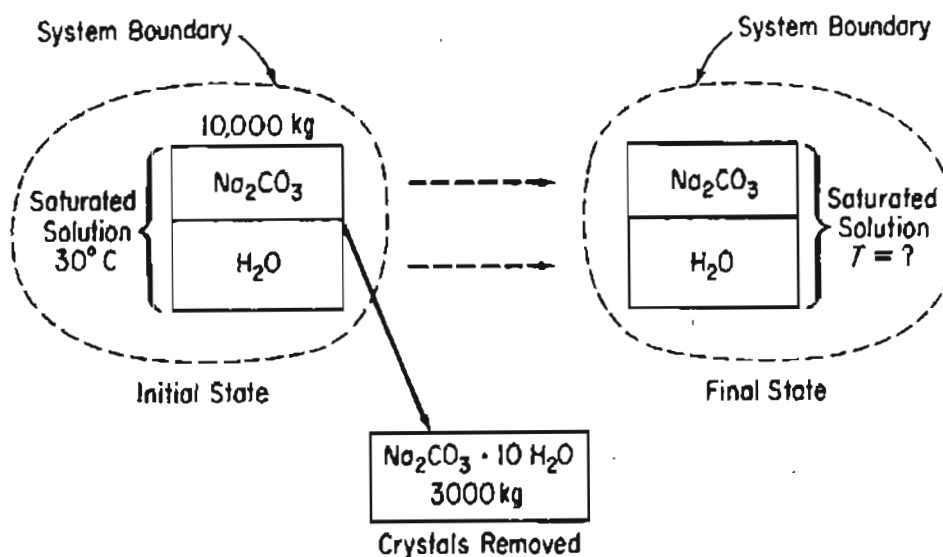


Figure E8.6a

Next, you need to get the compositions of the streams insofar as possible for each solution and the solid crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

Steps 2, 3, and 4

You definitely need solubility data for Na_2CO_3 as a function of the temperature:

Temp.(°C)	Solubility (g Na_2CO_3 /100 g H_2O)
0	7
10	12.5
20	21.5
30	38.8

Because the initial solution is saturated at 30°C, you can calculate the composition of the initial solution:

$$\frac{38.8 \text{ g Na}_2\text{CO}_3}{38.8 \text{ g Na}_2\text{CO}_3 + 100 \text{ g H}_2\text{O}} = 0.280 \text{ mass fraction Na}_2\text{CO}_3$$

Next, you should calculate the composition of the crystals.

Basis: 1 g mol $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

<u>Comp.</u>	<u>Mol</u>	<u>Mol wt.</u>	<u>Mass</u>	<u>Mass fr</u>
Na_2CO_3	1	106	106	0.371
H_2O	10	18	<u>180</u>	<u>0.629</u>
Total			286	1.00

Step 5

Select a basis. The following is convenient; others can be used, such as 3000 g of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$:

Basis: 10,000 kg of saturated solution at 30°C

Steps 2 and 3 (Repeated)

From the known data we have calculated the compositions of the compounds and solutions, and put them on Figure E8.6b. The problem now appears to be quite similar to the previous examples, particularly Example 8.4.

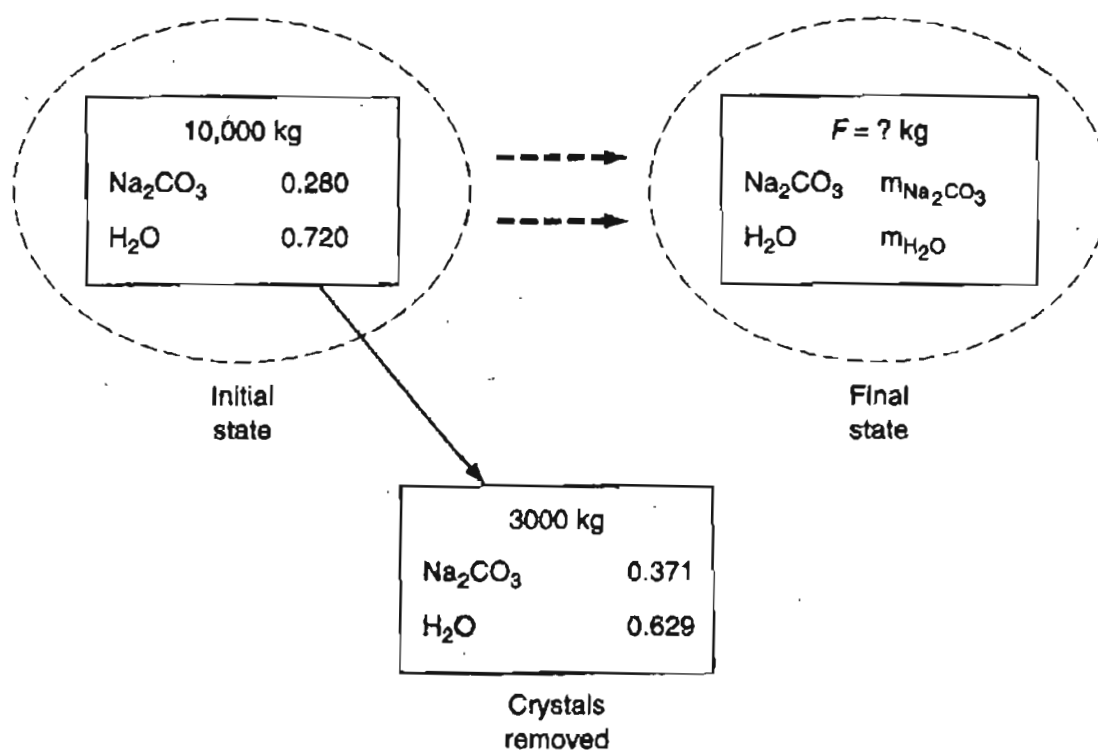


Figure E8.6b

Because we are treating this problem as an unsteady-state problem, the mass balance reduces to (the flow in = 0)

$$\text{accumulation} = \text{in} - \text{out}$$

Steps 6 and 7

The analysis of the degrees of freedom yields a value of zero (I stands for the initial, F the final state, and C the crystals).

Number of variables: 9

$$m_{\text{Na}_2\text{CO}_3}^I, m_{\text{H}_2\text{O}}^I, m_{\text{Na}_2\text{CO}_3}^F, m_{\text{H}_2\text{O}}^F, m_{\text{Na}_2\text{CO}_3}^C, m_{\text{H}_2\text{O}}^C, I, F, C$$

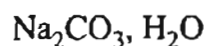
Number of equations: 9

Basis: $I = 10,000$ kg

Specifications:

$$\omega_{\text{Na}_2\text{CO}_3}^I, \omega_{\text{H}_2\text{O}}^I, \omega_{\text{Na}_2\text{CO}_3}^F, \omega_{\text{H}_2\text{O}}^F, \omega_{\text{Na}_2\text{CO}_3}^C, \omega_{\text{H}_2\text{O}}^C$$

Material balances:



Note that $\omega_i^I I = m_i^I$, $\omega_i^F F = m_i^F$, and $\omega_i^C C = m_i^C$ are redundant equations. For example, $m_{\text{Na}_2\text{CO}_3}^I$ could be replaced with $0.280I$ by using the specification for $\omega_{\text{Na}_2\text{CO}_3}^I$. Also redundant are equations such as $\sum \omega_i = 1$ and $\sum m_i = m_{\text{total}}$.

Steps 8 and 9

After substituting the specifications and basis into the material balances, (only two are independent) you get (in kg).

Accumulation in Tank					
	<u>Final</u>		<u>Initial</u>		<u>Transport out</u>
Na_2CO_3	$m_{\text{Na}_2\text{CO}_3}^F$	–	10,000(0.280)	=	–3000(0.371)
H_2O	$m_{\text{H}_2\text{O}}^F$	–	10,000(0.720)	=	–3000(0.629)
Total	F	–	10,000	=	–3000

The solution for the composition and amount of the final solution is

<u>Component</u>	<u>kg</u>
$m_{\text{Na}_2\text{CO}_3}^F$	1687
$m_{\text{H}_2\text{O}}^F$	5313
F (total)	7000

Step 10

Check using the total balance

$$7,000 + 3,000 = 10,000$$

To find the temperature of the final solution, calculate the composition of the final solution in terms of grams of Na_2CO_3 /100 grams of H_2O so that you can use the tabulated solubility data listed in Steps 2–4 above.

$$\frac{1,687 \text{ kg Na}_2\text{CO}_3}{5,313 \text{ kg H}_2\text{O}} = \frac{31.8 \text{ g Na}_2\text{CO}_3}{100 \text{ g H}_2\text{O}}$$

Thus, the temperature to which the solution must be cooled lies between 20°C and 30°C . By linear interpolation

$$30^\circ\text{C} - \frac{38.8 - 31.8}{38.8 - 21.5} (10.0^\circ\text{C}) = 26^\circ\text{C}$$

EXAMPLE 8.7 Hemodialysis

Hemodialysis is the most common method used to treat advanced and permanent kidney failure. When your kidneys fail, harmful wastes build up in your body, your blood pressure may rise, and your body may retain excess fluid and may not make enough red blood cells. In hemodialysis, your blood flows through a device with a special filter that removes wastes.

The dialyzer itself (refer to Figure E8.7a) is a large canister containing thousands of small fibers through which the blood passes.

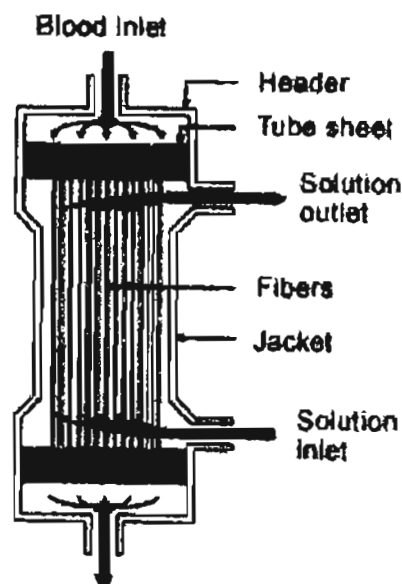


Figure E8.7a

Dialysis solution, the cleansing solution, is pumped around these fibers. The fibers allow wastes and extra fluids to pass from your blood into the solution that carries them away.

This example focuses on the plasma components of the streams: water, uric acid (UR), creatinine (CR), urea (U), P, K, and Na. You can ignore the initial filling of the dialyzer because the treatment lasts for an interval of two or three hours. Given the measurements obtained from one treatment shown in Figure E8.7b, calculate the grams per liter of each component of the plasma in the outlet solution.

Solution

This is an open steady-state system.

Step 5

Basis: 1 minute

Steps 3, 4, and 5

The data are inserted on Figure E8.7b.

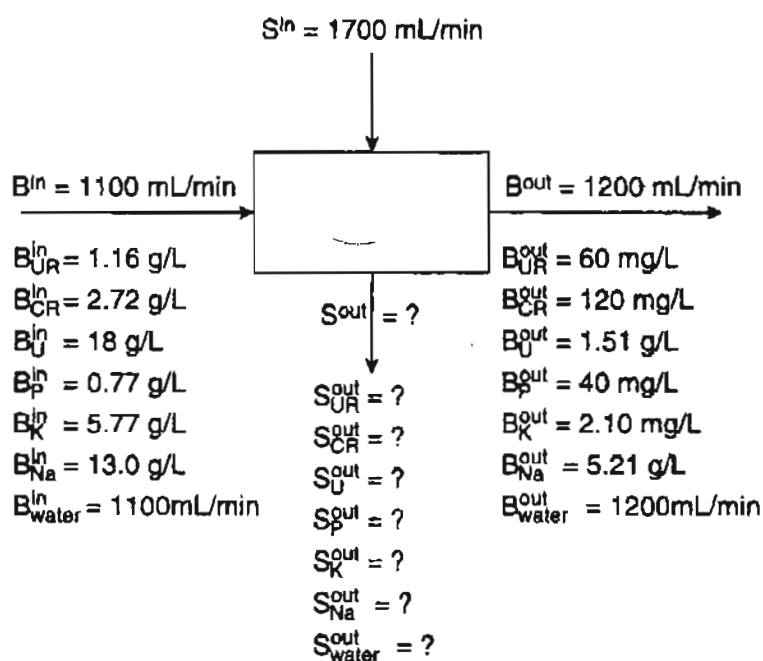


Figure E8.7b

You can ignore the effect of the components of the plasma on the density of the solution for this problem. The entering solution is assumed to be essentially water.

Steps 6 and 7

Number of unknowns (7): S_i^{out} for 7 components

Number of balances (7): 7 components

Degrees of freedom = 0

Steps 8 and 9

The water balance in grams, assuming that 1 mL is equivalent to 1 gram, is:

$$1100 + 1700 = 1200 + S_{\text{water}}^{\text{out}} \quad \text{hence:} \quad S_{\text{water}}^{\text{out}} = 1600 \text{ mL}$$

The component balances in grams are:

	<i>g/L</i>	
UR: $1.1(1.16) + 0 = 1.2(0.060) + 1.6 S_{\text{UR}}^{\text{out}}$	$S_{\text{UR}}^{\text{out}} = 0.75$	
CR: $1.1(2.72) + 0 = 1.2(0.120) + 1.6 S_{\text{CR}}^{\text{out}}$	$S_{\text{CR}}^{\text{out}} = 1.78$	
U: $1.1(18) + 0 = 1.2(1.51) + 1.6 S_{\text{U}}^{\text{out}}$	$S_{\text{U}}^{\text{out}} = 11.2$	
P: $1.1(0.77) + 0 = 1.2(0.040) + 1.6 S_{\text{P}}^{\text{out}}$	$S_{\text{P}}^{\text{out}} = 0.50$	
K: $1.1(5.77) + 0 = 1.2(0.120) + 16 S_{\text{K}}^{\text{out}}$	$S_{\text{K}}^{\text{out}} = 3.8$	
Na: $1.1(13.0) + 0 = 1.2(3.21) + 1.6 S_{\text{Na}}^{\text{out}}$	$S_{\text{Na}}^{\text{out}} = 6.53$	

Frequently Asked Questions

1. All of the examples presented have involved only a small set of equations to solve. If you have to solve a large set of equations, some of which may be redundant, how can you tell if the set of equations you select to solve is a set of *independent equations*? You can determine if the set is independent for linear equations by determining the rank of the coefficient matrix of the set of equations. Appendix L explains how to obtain the rank and shows some examples. Computer programs in Matlab, MathCad, Polymath, and so on provide a convenient way for you to determine the rank of the coefficient matrix without having to carry out the intermediate details of the calculations. Introduce the data into the computer program, and the output from the computer will provide you with some diagnostics if a solution is not obtained. For example, if the equations are not independent, Polymath returns the warning "Error—Singular matrix entered."
2. What should you do if the computer solution you obtain by solving a set of equations gives you a negative value for one or more of the unknowns? One possibility to examine is that you inadvertently reversed the sign of a term in a material balance, say from + to -. Another possibility is that you forgot to include an essential term(s) so that a zero was entered into the coefficient set for the equations rather than the proper number.

SELF-ASSESSMENT TEST

Questions

1. Answer the following questions true or false:
 - a. The most difficult part of solving material balance problems is the collection and formulation of the data specifying the compositions of the streams into and out of the system, and of the material inside the system.

- b. All open processes involving two components with three streams involve zero degrees of freedom.
 - c. An unsteady-state process problem can be analyzed and solved as a steady-state process problem.
 - d. If a flow rate is given in kg/min, you should convert it to kg mol/min.
2. Under what circumstances do equations or specifications become redundant?

Problems

1. A cellulose solution contains 5.2% cellulose by weight in water. How many kilograms of 1.2% solution are required to dilute 100 kg of the 5.2% solution to 4.2%?
2. A cereal product containing 55% water is made at the rate of 500 kg/hr. You need to dry the product so that it contains only 30% water. How much water has to be evaporated per hour?
3. If 100 g of Na_2SO_4 is dissolved in 200 g of H_2O and the solution is cooled until 100 g of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ crystallizes out, find (a) the composition of the remaining solution (the *mother liquor*) and (b) the grams of crystals recovered per 100 g of initial solution.
4. Salt in crude oil must be removed before the oil undergoes processing in a refinery. The crude oil is fed to a washing unit where freshwater fed to the unit mixes with the oil and dissolves a portion of the salt contained in the oil. The oil (containing some salt but no water), being less dense than the water, can be removed at the top of the washer. If the "spent" wash water contains 15% salt and the crude oil contains 5% salt, determine the concentration of salt in the "washed" oil product if the ratio of crude oil (with salt) to water used is 4:1.

Thought Problems

1. Although modern counterfeiters have mastered the duplication of the outside appearance of precious metals, some simple chemical/physical testing can determine their authenticity. Consult a reference book and determine the densities of gold, silver, copper, lead, iron, nickel, and zinc.
 - a. Could the density of pure gold be duplicated by using any of these metals?
 - b. Could the density of pure silver be duplicated by using any of these metals?
 - c. Assume that the volumes are conserved on mixing of the metals. What physical property makes any alloy an unlikely candidate for deception?
2. Incineration is one method of disposing of the sludge from sewage treatment plants. A lower limit for the combustion temperature exists to prevent odorous materials from remaining in the flue gas, and an upper limit exists to avoid melting the ash. High temperature operation of the incinerator will vaporize some of the heavy metals that cause air pollution. Thus, to prevent metals from vaporizing, it is preferable to operate at as low a temperature as possible.

In one run the following data were collected before and after combustion of the sludge.

	wt. % on a dry basis					mg/kg on a dry basis			
	Ash	Ig-loss	C	H	S	Cd	Pb	Cu	Zn
Sludge	67.0	33.0	15.1	2.2	1.1	169	412	384	1554
Residual ash	87.0	13.0	5.8	0	1.7	184	399	474	1943

Was the objective achieved of preventing vaporization of heavy metals?

Discussion Problems

1. Considerable concern has been expressed that the CO_2 generated from man's activities on earth has increased the CO_2 concentration in the atmosphere from 275 ppm in the last century to about 350 ppm currently. What are some of the important sources and sinks for CO_2 for the atmosphere on earth? Make a list. Estimate as best you can from news articles, books, and journals what the amount involved is for each source and sink. Estimate the accumulation of CO_2 per year in the atmosphere. Suggested references are *The Scientific American*, *Science*, *Nature*, *Chemical and Engineering News*, and various databases that can be accessed via CD disks and computer terminals.
2. Forests play an integral role in the dynamics of the global carbon cycle. Through photosynthesis, forests remove CO_2 from the atmosphere and accumulate some carbon over long periods of time. Decomposition of dead organic matter and fires release carbon back to the atmosphere. Tree harvesting also transfers carbon out of a forest. Prepare a report and figure(s) for the mass balance of carbon with a forest as the system. Include at a minimum growth, fire, mortality, harvesting, litter, decomposition, oxidation, and the soil and peat as components in the forest system. Designate pools of carbon that accumulate or are stable, and show the interface between the forest system and the surroundings (the atmosphere, sediments, usage by people, etc.).

Looking Back

In this chapter we explained via examples how to analyze problems involving material balances in the absence of chemical reactions. By using the 10-step procedure outlined in Chapter 7 we explained how the strategy can be used to solve each problem no matter what the process is.

GLOSSARY OF NEW WORDS

Tie component A component present in only one entering stream that exits only in one stream.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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<http://www2.ncsu.edu/unity/lockers/users/f/felder/public/Papers/205-KnowledgeStructure.pdf>

ANSWER TO THE PUZZLE

The magician held the egg 2.1 meters above the floor before dropping it.

PROBLEMS

- *8.1 You buy 100 kg of cucumbers that contain 99% water. A few days later they are found to be 98% water. Is it true that the cucumbers now only weigh 50 kg?

- *8.2 The fern *Pteris vittata* has been shown (*Nature*, 409, 579 (2001)) to effectively extract arsenic from soils. The study showed that in normal soil, which contains 6 ppm of arsenic, in two weeks the fern reduced the soil concentration to 5 ppm while accumulating 755 ppm of arsenic. In this experiment, what was the ratio of the soil mass to the plant mass? The initial arsenic in the fern was 5 ppm.
- *8.3 Sludge is wet solids that result from the processing in municipal sewage systems. The sludge has to be dried before it can be composted or otherwise handled. If a sludge containing 70% water and 30% solids is passed through a drier, and the resulting product contains 25% water, how much water is evaporated per ton of sludge sent to the drier.
- *8.4 Figure P8.4 is a sketch of an artificial kidney, a medical device used to remove waste metabolites from your blood in cases of kidney malfunction. The dialyzing fluid passes across a hollow membrane, and the waste products diffuse from the blood into the dialyzing fluid.

If the blood entering the unit flows at the rate of 220 mL/min, and the blood exiting the unit flows at the rate of 215 mL/min, how much water and urea (the main waste product) pass into the dialysate if the entering concentration of urea is 2.30 mg/mL and the exit concentration of urea is 1.70 mg/L?

If the dialyzing fluid flows into the unit at the rate of 100 mL/min, what is the concentration of the urea in the dialysate?

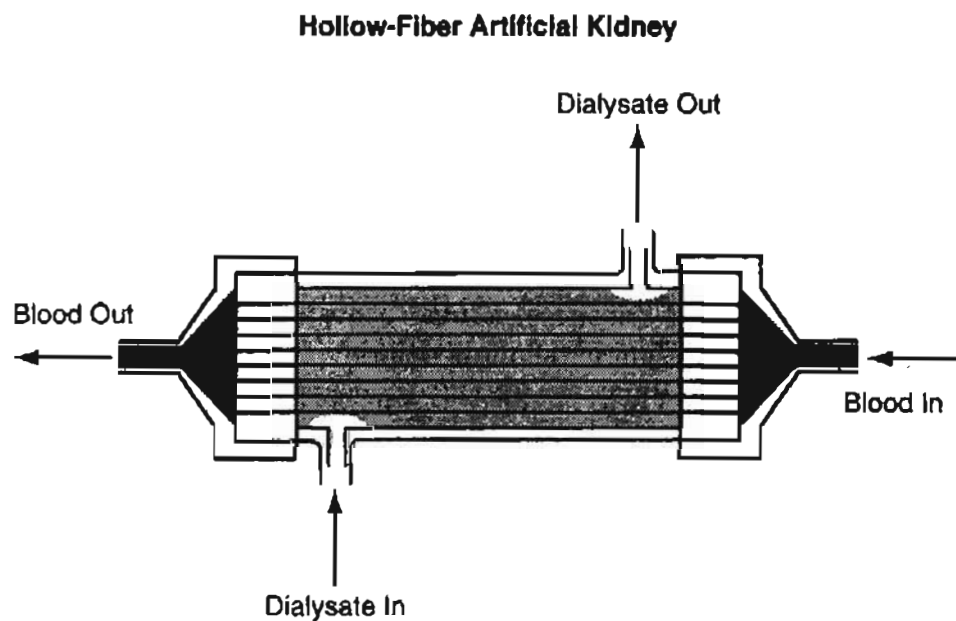


Figure P8.4

- *8.5 A multiple stage evaporator concentrates a weak NaOH solution from 3% to 18%, and processes 2 tons of solution per day. How much product is made per day? How much water is evaporated per day?
- *8.6 A liquid adhesive consists of a polymer dissolved in a solvent. The amount of polymer in the solution is important to the application. An adhesive dealer receives an

order for 3000 pounds of an adhesive solution containing 13% polymer by weight. On hand is 500 pounds of 10% solution and very large quantities of 20% solution and pure solvent. Calculate the weight of each that must be blended together to fill this order. Use all of the 10% solution.

- *8.7 A lacquer plant must deliver 1000 lb of an 8% nitrocellulose solution. They have in stock a 5.5% solution. How much dry nitrocellulose must be dissolved in the solution to fill the order?
- ✓*8.8 A gas containing 80% CH_4 and 20% He is sent through a quartz diffusion tube (see Figure P8.8) to recover the helium. Twenty percent by weight of the original gas is recovered, and its composition is 50% He. Calculate the composition of the waste gas if 100 kg moles of gas are processed per minute.

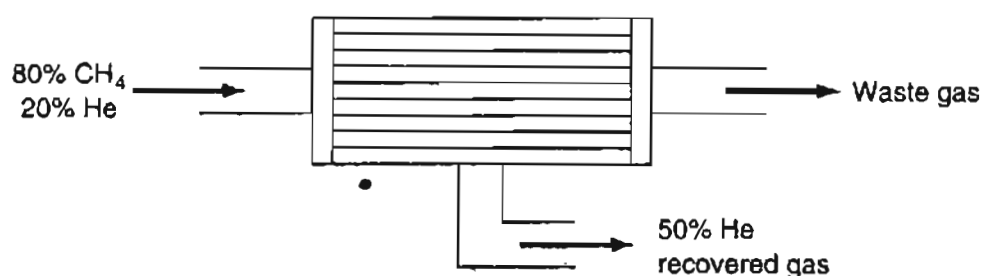


Figure P8.8

- *8.9 In many fermentations, the maximum amount of cell mass must be obtained. However, the amount of mass that can be made is ultimately limited by the cell volume. Cells occupy a finite volume and have a rigid shape so that they cannot be packed beyond a certain limit. There will always be some water remaining in the interstices between the adjacent cells, which represents the void volume that at best can be as low as 40% of the fermenter volume. Calculate the maximum cell mass on a dry basis per L of the fermenter that can be obtained if the wet cell density is 1.1 g/cm^3 . Note that cells themselves consist of about 75% water and 25% solids, and cell mass is reported as dry weight in the fermentation industry.
- *8.10 A polymer blend is to be formed from the three compounds whose compositions and approximate formulas are listed in the table. Determine the percentages of each compound A, B, and C to be introduced into the mixture to achieve the desired composition.

Composition	Compound (%)			Desired mixture
	A	B	C	
$(\text{CH}_4)_x$	25	35	55	30
$(\text{C}_2\text{H}_6)_x$	35	20	40	30
$(\text{C}_3\text{H}_8)_x$	40	45	5	40
Total	100	100	100	100

How would you decide to blend compounds A, B, C, and D [$(\text{CH}_4)_x = 10\%$, $(\text{C}_2\text{H}_6)_x = 30\%$, $(\text{C}_3\text{H}_8)_x = 60\%$] to achieve the desired mixture?

- *8.11** Your boss asks you to calculate the flow through a natural-gas pipeline. Since it is 26 in. in diameter, it is impossible to run the gas through any kind of meter or measuring device. You decide to add 100 lb of CO_2 per minute to the gas through a small 1/2-in. piece of pipe, collect samples of the gas downstream, and analyze them for CO_2 . Several consecutive samples after 1 hr are

<i>time</i>	<i>% CO_2</i>
1 hr, 0 min	2.0
10 min	2.2
20 min	1.9
30 min	2.1
40 min	2.0

- (a) Calculate the flow of gas in pounds per minute at the point of injection.
(b) Unfortunately for you, the gas upstream of the point of injection of CO_2 already contained 1.0 percent CO_2 . How much was your original flow estimate in error (in percent)?

Note: In part (a) the natural gas is all methane, CH_4 .

- *8.12** Ammonia is a gas for which reliable analytical methods are available to determine its concentration in other gases. To measure flow in a natural gas pipeline, pure ammonia gas is injected into the pipeline at a constant rate of 72.3 kg/min for 12 min. Five miles downstream from the injection point, the steady-state ammonia concentration is found to be 0.382 weight percent. The gas upstream from the point of ammonia injection contains no measurable ammonia. How many kilograms of natural gas are flowing through the pipelines per hour?
- *8.13** Water pollution in the Hudson River has claimed considerable recent attention, especially pollution from sewage outlets and industrial wastes. To determine accurately how much effluent enters the river is quite difficult because to catch and weigh the material is impossible, weirs are hard to construct, and so on. One suggestion that has been offered is to add a tracer of Br ion to a given sewage stream, let it mix well, and sample the sewage stream after it mixes. On one test of the proposal you add ten pounds of NaBr per hour for 24 hours to a sewage stream with essentially no Br in it. Somewhat downstream of the introduction point a sampling of the sewage stream shows 0.012% NaBr. The sewage density is 60.3 lb/ft³ and river water density is 62.4 lb/ft³. What is the flow rate of the sewage in lb/min?
- *8.14** A new process for separating a mixture of incompatible polymers, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), promises to expand the recycling and reuse of plastic waste. The first commercial plant, at Celanese's recycling facility in Spartanburg, S.C., has been operating since February at a PET capacity of 15 million lb/yr. Operating cost: 0.5¢/lb.

Targeted to replace the conventional sorting of individual PET bottles from PVC containers upstream of the recycling step, this process first chops the mixed waste with a rotary-blade cutter to 0.5-in. chips. The materials are then suspended in water, and air is forced through to create a bubble-like froth that preferentially entraps the PVC be-

cause of its different surface-tension characteristics. A food-grade surfactant is also added to enhance the separation. The froth is skimmed away along with the PVC, leaving behind the PET material. For a feed with 2% PVC, the process has recovered almost pure PET with an acceptable PVC contamination level of 10 ppm

How many lb of PVC are recovered per year from the above cited process?

- *8.15** If 100 g of Na_2SO_4 is dissolved in 200 g of H_2O and the solution is cooled until 100 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallizes out, find
- The composition of the remaining solution (*mother liquor*).
 - The grams of crystals recovered per 100 g of initial solution.
- *8.16** A chemist attempts to prepare some very pure crystals of borax (sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) by dissolving 100g of $\text{Na}_2\text{B}_4\text{O}_7$ in 200 g of boiling water. He then carefully cools the solution slowly until some $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystallizes out. Calculate the g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ recovered in the crystals per 100 g of total initial solution ($\text{Na}_2\text{B}_4\text{O}_7$ plus H_2O), if the residual solution at 55°C after the crystals are removed contains 12.4% $\text{Na}_2\text{B}_4\text{O}_7$.
- *8.17** 1000 kg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are added to a mixture of crystals of $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ to produce a mixture of $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$ crystals. How much $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ must be added to produce the most $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$?
- *8.18** The solubility of barium nitrate at 100°C is 34 g/100 g of H_2O and at 0°C is 5.0 g/100 g of H_2O . If you start with 100 g of $\text{Ba}(\text{NO}_3)_2$ and make a saturated solution in water at 100°C , how much water is required? If the saturated solution is cooled to 0°C , how much $\text{Ba}(\text{NO}_3)_2$ is precipitated out of solution? The precipitated crystals carry along with them on their surface 4 g of H_2O per 100 g of crystals.
- *8.19** A water solution contains 60% $\text{Na}_2\text{S}_2\text{O}_3$ together with 1% soluble impurity. Upon cooling to 10°C , $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystallizes out. The solubility of this hydrate is 1.4 lb $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ /lb free water. The crystals removed carry as adhering solution 0.06 lb solution/lb crystals. When dried to remove the remaining water (but not the water of hydration), the final dry $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystals must not contain more than 0.1 % impurity. To meet this specification, the original solution, before cooling, is further diluted with water. On the basis of 100 lb of the original solution, calculate:
- The amount of water added before cooling.
 - The percentage recovery of the $\text{Na}_2\text{S}_2\text{O}_3$ in the dried hydrated crystals.
- *8.20** Paper pulp is sold on the basis that it contains 12 percent moisture; if the moisture exceeds this value, the purchaser can deduct any charges for the excess moisture and also deduct for the freight costs of the excess moisture. A shipment of pulp became wet and was received with a moisture content of 22 percent. If the original price for the pulp was \$40/ton of air-dry pulp and if the freight is \$1.00/100 lb shipped, what price should be paid per ton of pulp delivered?
- *8.21** A laundry can purchase soap containing 30% water for a price of \$0.30/kg fob the soap manufacturing plant (i.e., at the soap plant before shipping costs which are owed by the purchaser of the soap). It can also purchase a different grade of soap that contains only 5% water. The freight rate between the soap plant and the laundry is \$6.05/100 kg. What is the maximum price the laundry should pay for the 5% soap?

- ✓**8.22
3.25 A manufacturer of briquets has a contract to make briquets for barbecuing that are guaranteed to not contain over 10% moisture or 10% ash. The basic material they use has the analysis: moisture 12.4%, volatile material 16.6%, carbon 57.5%, and ash 13.5%. To meet the specifications (at their limits) they plan to mix with the base material a certain amount of petroleum coke that has the analysis: volatile material 8.2%, carbon 88.7%, and moisture 3.1%. How much petroleum coke must be added per 100 lb of the base material?

- **8.23 In a gas-separation plant, the feed to the process has the following constituents:

Component	Mole %
C ₃	1.9
<i>i</i> -C ₄	51.5
<i>n</i> -C ₄	46.0
C ₅ ⁺	0.6
Total	100.0

The flow rate is 5804 kg mol/day. If the overhead and bottoms streams leaving the process have the following compositions, what are the flow rates of the overhead and bottoms streams in kg mol/day?

Component	Mole %	
	Overhead	Bottoms
C ₃	3.4	—
<i>i</i> -C ₄	95.7	1.1
<i>n</i> -C ₄	0.9	97.6
C ₅ ⁺	—	1.3
Total	100.0	100.0

- **8.24 The organic fraction in the wastewater is measured in terms of the biological oxygen demand (BOD) material, namely the amount of dissolved oxygen required to biodegrade the organic contents. If the dissolved oxygen (DO) concentration in a body of water drops too low, the fish in the stream or lake may die. The Environmental Protection Agency has set the minimum summer levels for lakes at 5 mg/L of DO.
- (a) If a stream is flowing at 0.3 m³/s and has an initial BOD of 5 mg/L before reaching the discharge point of a sewage treatment plant, and the plant discharges 3.785 ML/day of wastewater, with a concentration of 0.15 g/L of BOD, what will be the BOD concentration immediately below the discharge point of the plant?
- (b) The plant reports a discharge of 15.8 ML/day having a BOD of 72.09 mg/L. If the EPA measures the flow of the stream before the discharge point at 530 ML/day with 3 mg/L of BOD, and measures the downstream concentration of 5 mg/L of BOD, is the report correct? ✓
- **8.25 Suppose that 100 L/min are drawn from a fermentation tank and passed through an extraction tank in which the fermentation product (in the aqueous phase) is mixed with an organic solvent, and then the aqueous phase is separated from the organic

phase. The concentration of the desired enzyme (3-hydroxybutyrate dehydrogenase) in the aqueous feed to the extraction tank is 10.2 g/L. The pure organic extraction solvent runs into the extraction tank at the rate of 9.5 L/min. If the ratio of the enzyme in the exit product stream (the organic phase) from the extraction tank to the concentration of the enzyme in the exit waste stream (the aqueous phase) from the tank is $D = 18.5$ (g/L organic)/(g/L aqueous), what is the fraction recovery of the enzyme and the amount recovered per min? Assume negligible miscibility between the aqueous and organic liquids in each other, and ignore any change in density on removal or addition of the enzyme to either stream.

- ✓***8.26 Consider the following process for recovering NH_3 from a gas stream composed of N_2 and NH_3 (see Figure P8.26).

Flowing upward through the process is the gas stream, which can contain NH_3 and N_2 but *not* solvent S, and flowing downward through the device is a liquid stream which can contain NH_3 and liquid S but *not* N_2 .

The weight fraction of NH_3 in the gas stream A leaving the process is related to the weight fraction of NH_3 in the liquid stream B leaving the process by the following empirical relationship: $\omega_{\text{NH}_3}^A = 2\omega_{\text{NH}_3}^B$.

Given the data shown in Figure P8.26, calculate the flow rates and compositions of streams A and B.

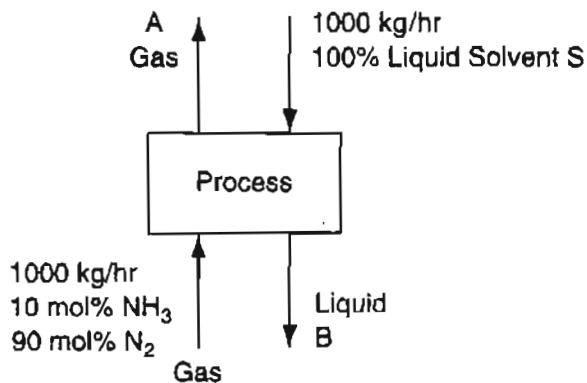


Figure P8.26

- *8.27 MTBE (methyl tertiary butyl ether) is added to gasoline to increase the oxygen content of the gasoline. MTBE is soluble in water to some extent, and becomes a contaminant when the gasoline gets into surface or underground water. The gasoline used by boats has an MTBE content of 10%. The boats operate in a well-mixed flood control pond having the dimensions 3 km long, 1 km wide, and 3 m deep on the average. Suppose that each of the 25 boats on the pond spill 0.5 L of gasoline during 12 hours of daylight. The flow of water (that contains no MTBE) into the pond is $10 \text{ m}^3/\text{hr}$, but no water leaves because the water level is well below the spillway of the pond. By how much will the concentration of MTBE increase in the pond after the end of 12 hours of boating? Data: The specific gravity of gasoline is 0.72.

CHAPTER 9

THE CHEMICAL REACTION EQUATION AND STOICHIOMETRY

9.1 Stoichiometry

226

9.2 Terminology for Applications of Stoichiometry

233

Your objectives in studying this chapter are to be able to:

1. Write and balance chemical reaction equations.
2. Identify the products for common reactions given the reactants.
3. Determine the stoichiometric quantities of reactants and products in moles or mass given the chemical reaction.
4. Define excess reactant, limiting reactant, conversion, degree of completion, selectivity, yield, and extent of a reaction.
5. Identify the limiting and excess reactants in a reaction, and calculate the fraction or percent excess reactant(s), the percent conversion or completion, the yield, and the extent of reaction with the reactants given in nonstoichiometric proportions.

What is there about stoichiometry that makes the topic worth reviewing at this time? You need a solid grasp of what the chemical reaction equations imply before applying them to material and energy balances. This chapter will help you enhance your understanding of this important area.

Looking Ahead

In this chapter we review some of the concepts related to chemical reactions, and define and apply a number of terms associated with complete and incomplete reactions.

225

9.1 Stoichiometry

You are probably aware that chemical engineers in practicing their profession differ from most other engineers because of their involvement with chemistry. When chemical reactions occur, in contrast with physical changes of material such as evaporation or dissolution, you want to be able to predict the mass or moles required for the reaction(s), and the mass or moles of each species remaining after the reaction has occurred. Reaction stoichiometry allows you to accomplish this task. The word **stoichiometry** (stoi-ki-om-e-tri) derives from two Greek words: *stoicheion* (meaning "element") and *metron* (meaning "measure"). Stoichiometry provides a quantitative means of relating the amount of products produced by chemical reaction(s) to the amount of reactants.

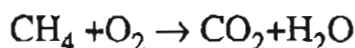
As you already know, the chemical reaction equation provides both qualitative and quantitative information concerning chemical reactions. Specifically the chemical reaction equation provides you with information of two types:

1. It tells you what substances are reacting (those being used up) and what substances are being produced (those being made).
2. The coefficients of a balanced equation tell you what the mole ratios are among the substances that react or are produced. (In 1803, John Dalton, an English chemist, was able to explain much of the experimental results on chemical reactions of the day by assuming that reactions occurred with fixed ratios of elements.)

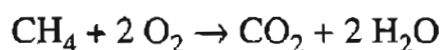
A chemical reaction may not occur as rapidly as the combustion of natural gas in a furnace, such as, for example, in the slow oxidation of your food, but if the reaction occurs (or would occur), it takes place as represented by a chemical reaction equation.

You should take the following steps in solving stoichiometric problems:

1. Make sure the chemical equation is correctly balanced. How do you tell if the reaction equation is balanced? Make sure the total quantities of each of the elements on the lefthand side equal those on the righthand side. For example,



is not a balanced stoichiometric equation because there are four atoms of H on the reactant side (lefthand side) of the equation, but only two on the product side (righthand side). In addition, the oxygen atoms do not balance. The balanced equation is given by

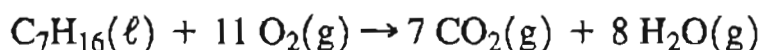


The coefficients in the balanced reaction equation have the units of moles of a species reacting or produced relative to the other species reacting for the particu-

lar reaction equation. If you multiply each term in a chemical reaction equation by the same constant, say two, the absolute stoichiometric coefficient in each term doubles, but the coefficients still exist in the same relative proportions.

2. Use the proper degree of completion for the reaction. If you do not know how much reaction has occurred, you have to assume some amount, such as complete reaction.
3. Use molecular weights to convert mass to moles for the reactants and products, and vice versa.
4. Use the coefficients in the chemical equation to obtain the molar amounts of products produced and reactants consumed by the reaction.

Steps 3 and 4 can be applied in a fashion similar to that used in carrying out the conversion of units as explained in Chapter 1. As an example, the combustion of heptane takes place according to the following reaction equation



(Note that we have put the states of the compounds in parentheses after the species formula, information not needed for this chapter, but that will be vital in Parts 3 and 4 of this book.)

What can you learn from a chemical reaction equation? The **stoichiometric coefficients** in the chemical reaction equation (1 for C_7H_{16} , 11 for O_2 , and so on) tell you the relative amounts of moles of chemical species that react and are produced by the reaction. The units of a stoichiometric coefficient for species i are the change in the moles of species i divided by the moles reacting according to the specific chemical equation. We will abbreviate the units simply as mol i /moles reacting when appropriate, but frequently in practice the units of moles reacting are ignored. You can conclude that 1 mole (*not* lb_m or kg) of heptane will react with 11 moles of oxygen to give 7 moles of carbon dioxide plus 8 moles of water. These may be lb mol, g mol, kg mol, or any other type of mole. Another way to use the chemical reaction equation is to indicate that 1 mole of CO_2 is formed from each $\frac{1}{7}$ mole of C_7H_{16} , and 1 mole of H_2O is formed with each $\frac{7}{8}$ mole of CO_2 . The latter ratios indicate the use of **stoichiometric ratios** in determining the relative proportions of products and reactants.

Suppose you are asked how many kg of CO_2 will be produced as the product if 10 kg of C_7H_{16} react completely with the **stoichiometric quantity** of O_2 ? On the basis of 10 kg of C_7H_{16}

$$\frac{10 \text{ kg C}_7\text{H}_{16}}{1} \left| \frac{1 \text{ kg mol C}_7\text{H}_{16}}{100.1 \text{ kg C}_7\text{H}_{16}} \right| \left| \frac{7 \text{ kg mol CO}_2}{1 \text{ kg mol C}_7\text{H}_{16}} \right| \left| \frac{44.0 \text{ kg CO}_2}{1 \text{ kg mol CO}_2} \right| = 30.8 \text{ kg CO}_2$$

EXAMPLE 9.1 Balancing a Reaction Equation for a Biological Reaction

The primary energy source for cells is the aerobic catabolism (oxidation) of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, a sugar). The overall oxidation of glucose produces CO_2 and H_2O by the following reaction



Determine the values of a , b , and c that balance this chemical reaction equation.

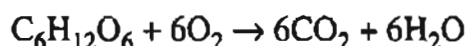
Solution

Basis: The given reaction

By inspection, the carbon balance gives $b = 6$, the hydrogen balance gives $c = 6$, and an oxygen balance

$$6 + 2a = 6 \times 2 + 6$$

gives $a = 6$. Therefore, the balanced equation is



Let's now write a general chemical reaction equation as



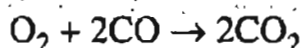
where a , b , c , and d are the stoichiometric coefficients for the species A , B , C , and D , respectively. Equation (9.1) can be written in a general form

$$\nu_A A + \nu_B B + \nu_C C + \nu_D D = \sum \nu_i S_i = 0 \quad (9.2)$$

where ν_i is the stoichiometric coefficient for species S_i . The products are defined to have positive values for coefficients and the reactants to have negative values for coefficients. The ratios are unique for a given reaction. Specifically in Equation (9.1)

$$\begin{aligned} \nu_C &= -c & \nu_A &= a \\ \nu_D &= -d & \nu_B &= b \end{aligned}$$

If a species is not in an equation, the value of its stoichiometric coefficient is deemed to be zero. As an example, in the reaction



$$\nu_{\text{O}_2} = -1 \quad \nu_{\text{CO}} = -2 \quad \nu_{\text{CO}_2} = 2 \quad \nu_{\text{N}_2} = 0$$

EXAMPLE 9.2 Use of the Chemical Equation to Calculate the Mass of Reactants Given the Mass of Products

In the combustion of heptane, CO_2 is produced. Assume that you want to produce 500 kg of dry ice per hour, and that 50% of the CO_2 can be converted into dry ice, as shown in Figure E9.2. How many kilograms of heptane must be burned per hour?

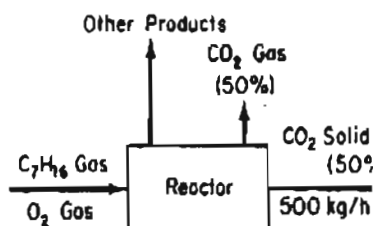


Figure E9.2

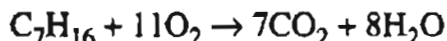
Solution

In solving a problem of this sort, the grand thing is to be able to reason backward. This is a very useful accomplishment, and a very easy one, but people do not practice it much.

Sherlock Holmes, in *Sir Arthur Conan Doyle's*
a Study in Scarlet

From the problem statement you can conclude that you want to use the product mass of CO_2 to calculate a reactant mass, the C_7H_{16} . The procedure is first to convert kilograms of CO_2 to moles, apply the chemical equation to get moles of C_7H_{16} , and finally calculate the kilograms of C_7H_{16} . We will use Figure E9.2 in the analysis.

Look in Appendix D1 to get the molecular weights of CO_2 (44.0) and C_7H_{16} (100.1). The chemical equation is



The next step is to select a basis.

Basis: 500 kg of dry ice (equivalent to 1 hr)

The calculation of the amount of C_7H_{16} can be made in one sequence:

$$\begin{aligned} \frac{500 \text{ kg dry ice}}{0.5 \text{ kg dry ice}} & \left| \frac{1 \text{ kg CO}_2}{44.0 \text{ kg CO}_2} \right| \left| \frac{1 \text{ kg mol CO}_2}{7 \text{ kg mol CO}_2} \right| \left| \frac{1 \text{ kg mol C}_7\text{H}_{16}}{100.1 \text{ kg C}_7\text{H}_{16}} \right| \\ & = 325 \text{ kg C}_7\text{H}_{16} \end{aligned}$$

Finally, you should check your answer by reversing the sequence of calculations.

EXAMPLE 9.3 Application of Stoichiometry When More than One Reaction Occurs

A limestone analyses (weight %)

CaCO ₃	92.89%
MgCO ₃	5.41%
Inert	1.70%

By heating the limestone you recover oxides known as lime.

- (a) How many pounds of calcium oxide can be made from 1 ton of this limestone?
- (b) How many pounds of CO₂ can be recovered per pound of limestone?
- (c) How many pounds of limestone are needed to make 1 ton of lime?

Solution**Steps 1, 2, and 3**

Read the problem carefully to fix in mind exactly what is required. The carbonates are decomposed to oxides. You should recognize that lime (oxides of Ca and Mg) will also include other inert compounds present in the limestone that remain after the CO₂ has been driven off.

Step 2

Next, draw a picture of what is going on in this process. See Figure E9.3.

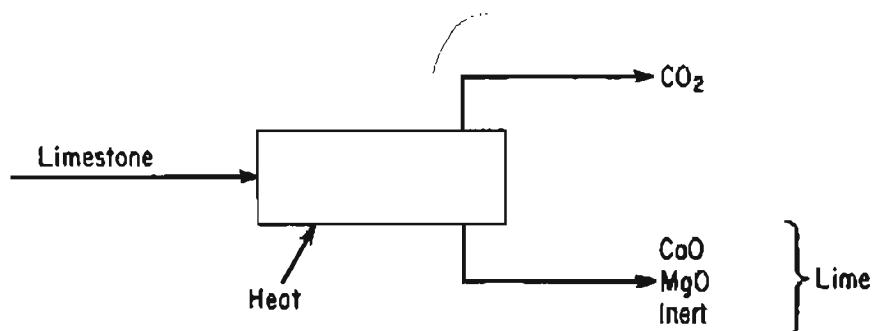


Figure E9.3

Step 4

To complete the preliminary analysis you need the following chemical equations:



Additional data that you need to look up (or calculate) are the molecular weights of the species

	CaCO ₃	MgCO ₃	CaO	MgO	CO ₂
Mol. Wt.:	100.1	84.32	56.08	40.32	44.0

Step 5

The next step is to pick a basis:

Basis: 100 lb of limestone

This basis was selected because pounds will be equal to percent. You could also pick 1 lb of limestone if you wanted, or 1 ton.

Steps 6, 7, 8, and 9

Calculations of the percent composition and lb moles of the limestone and products in the form of a table will serve as an adjunct to Figure E9.3, and will prove to be most helpful in answering the questions posed.

Limestone			Solid Products		
Component	lb = percent	lb mol	Compound	lb mol	lb
CaCO ₃	92.89	0.9280	CaO	0.9280	52.04
MgCO ₃	5.41	0.0642	MgO	0.0642	2.59
Inert	1.70		Inert		1.70
Total	100.00	0.9920	Total	0.9920	56.33

The quantities listed under Products are calculated from the chemical equations. For example, for the last column:

$$\frac{92.89 \text{ lb CaCO}_3}{100.1 \text{ lb CaCO}_3} \left| \frac{1 \text{ lb mol CaCO}_3}{1 \text{ lb mol CaCO}_3} \right| \frac{1 \text{ lb mol CaO}}{1 \text{ lb mol CaCO}_3} \left| \frac{56.08 \text{ lb CaO}}{1 \text{ lb mol CaO}} \right| = 52.04 \text{ lb CaO}$$

$$\frac{5.41 \text{ lb MgCO}_3}{84.32 \text{ lb MgCO}_3} \left| \frac{1 \text{ lb mol MgCO}_3}{1 \text{ lb mol MgCO}_3} \right| \frac{1 \text{ lb mol MgO}}{1 \text{ lb mol MgCO}_3} \left| \frac{40.32 \text{ lb MgO}}{1 \text{ lb mol MgO}} \right| = 2.59 \text{ lb MgO}$$

The production of CO₂ is:

$$\begin{array}{l} 0.9280 \text{ lb mol CaO is equivalent to } 0.9280 \text{ lb mol CO}_2 \\ 0.0642 \text{ lb mol MgO is equivalent to } 0.0642 \text{ lb mol CO}_2 \\ \hline \text{Total} \qquad \qquad \qquad 0.992 \text{ lb mol CO}_2 \end{array}$$

$$\frac{0.992 \text{ lb mol CO}_2}{1 \text{ lb mol CO}_2} \left| \frac{44.0 \text{ lb CO}_2}{1 \text{ lb mol CO}_2} \right| = 44.65 \text{ lb CO}_2$$

Alternately, you could have calculated the lb CO₂ from a total balance: 100 - 56.33 = 44.67. Note that the total pounds of all of the products equal the 100 lb of entering limestone. If it did not, what would you do? Check your molecular weight values and your calculations.

Now, to calculate the quantities originally asked for:

$$(a) \text{ CaO produced} = \frac{52.04 \text{ lb CaO}}{100 \text{ lb limestone}} \left| \frac{2000 \text{ lb}}{1 \text{ ton}} \right| = 1041 \text{ lb CaO/ton}$$

$$(b) \text{ CO}_2 \text{ recovered} = \frac{43.65 \text{ lb CO}_2}{100 \text{ lb limestone}} = 0.437 \text{ lb CO}_2/\text{lb limestone}$$

$$(c) \text{ Limestone required} = \frac{100 \text{ lb limestone}}{56.33 \text{ lb lime}} \left| \frac{2000 \text{ lb}}{1 \text{ ton}} \right| = 3550 \text{ lb limestone/ton lime}$$

SELF-ASSESSMENT TEST

Question

1. For the following reaction



a student wrote the following to determine how many moles of MnO_4^- would react with 3 moles of Fe^{2+} :

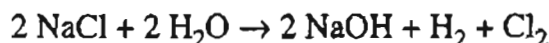
1 mol $\text{MnO}_4^- = 5 \text{ mol Fe}^{2+}$. Divide both sides by 5 mol Fe^{2+} to get 1 mol $\text{MnO}_4^-/5 \text{ mol Fe}^{2+} = 1$. The number of mol of MnO_4^- that reacts with 3 mol of Fe^{2+} is

$$\frac{1 \text{ mol MnO}_4^-}{5 \text{ mol Fe}^{2+}} (3 \text{ mol Fe}^{2+}) = 0.6 \text{ mol MnO}_4^-$$

Is the calculation correct?

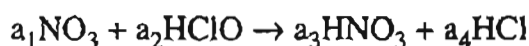
Problems

- Write balanced reaction equations for the following reactions:
 - C_9H_{18} and oxygen to form carbon dioxide and water.
 - FeS_2 and oxygen to form Fe_2O_3 and sulfur dioxide.
- If 1 kg of benzene (C_6H_6) is oxidized with oxygen, how many kilograms of O_2 are needed to convert all the benzene to CO_2 and H_2O ?
- The electrolytic manufacture of chlorine gas from a sodium chloride solution is carried out by the following reaction:



How many kilograms of Cl_2 can be produced from 10 m³ of brine solution containing 5% by weight of NaCl? The specific gravity of the solution relative to that of water at 4°C is 1.07.

4. Can you balance the following chemical reaction equation?



Thought Problems

1. An accident occurred in which one worker lost his life. A large steel evaporator in magnesium chloride service, containing internal heating tubes, was to be cleaned. It was shut down, drained, and washed. The next day two employees who were involved in the maintenance of the evaporator entered the vessel to repair the tubes. They were overcome, apparently from lack of oxygen. Subsequently, one employee recovered and escaped, but the other never regained consciousness, and died several days later.

What in your opinion might have caused the accident (the lack of oxygen)?

2. A magazine reported that to degrade crude oil in a spill in seawater the oil-degrading bacteria require the dissolved oxygen in over 300,000 gal of air-saturated seawater to break down just 1 gal of crude. Can this estimate be correct?
3. An article advocating the planting of trees explains that a tree can assimilate 13 lb of carbon dioxide per year, or enough to offset the CO_2 produced by driving one car 26,000 miles per year. Can this statement be correct?

Discussion Problems

1. Pollutants from diesel fuel pose a threat to the respiratory tract and are a potential cause of cancer according to the Environmental Protection Agency. The Clean Air Act of 1990 required that the sulfur content of diesel fuel used on freeways must be lowered from 0.30 percent by weight to 0.05 percent—a substantial reduction.

How might this be accomplished economically? At the oil well, at the refinery, at the service station, in the car, or what?

9.2 Terminology for Applications of Stoichiometry

Nothing is like it seems but everything is like it is.

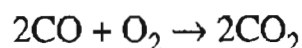
Yogi Berra

So far we have discussed the stoichiometry of reactions in which the proper stoichiometric ratio of reactants are fed into a reactor, and the reaction goes to completion. Subsequently, no reactants remain in the reactor. What if (a) some other ratio of reactants is fed, or (b) the reaction is incomplete? In such circumstances you need to be familiar with a number of terms you will encounter in solving various types of problems.

9.2-1 Extent of Reaction

You will find the **extent of reaction** useful in solving material balances involving chemical reaction. The extent of reaction, ξ , is based on a particular stoi-

chiometric equation, and denotes how much reaction occurs. Its units are "moles reacting." The extent of reaction is calculated by dividing the change in the number of moles of a species that occurs in a reaction, for either a reactant or a product, by the related stoichiometric coefficient. For example, consider the chemical reaction equation for the combustion of carbon monoxide



The signs of the stoichiometric coefficients to be used will conform to what is standard practice in calculating the extent of reaction, namely the products of the reaction have positive signs and the reactants have negative signs.

If 20 moles of CO are fed to a reactor with 10 moles of O₂ and form 15 moles of CO₂, the extent of reaction can be calculated from the amount of CO₂ that is produced

The value of the change in the moles of CO₂ is: 15 - 0 = 15.

The value of the stoichiometric coefficient for the CO₂ is 2 mol/mol reacting.

Then the extent of reaction is:

$$\frac{(15 - 0) \text{ mol CO}_2}{2 \text{ mol CO}_2 / \text{moles reacting}} = 7.5 \text{ moles reacting}$$

Let's next consider a more formal definition of the extent of reaction, one that takes into account incomplete reaction, and involves the initial concentrations of reactants and products. The extent of reaction is defined as follows:

$$\xi = \frac{n_i - n_{i0}}{\nu_i} \quad (9.3)$$

where n_i = moles of species i present in the system after the reaction occurs

n_{i0} = moles of species i present in the system when the reaction starts

ν_i = coefficient for species i in the particular chemical reaction

equation (moles of species i produced or consumed per moles reacting)

ξ = extent of reaction (moles reacting)

The coefficients of the products in a chemical reaction are assigned positive values and the reactants assigned negative values. Note that $(n_i - n_{i0})$ is equal to the generation or consumption of component i by reaction.

Equation (9.3) can be rearranged to calculate the number of moles of component i from the value of the extent of reaction

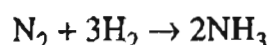
$$n_i = n_{i0} + \xi \nu_i \quad (9.4)$$

As shown in the next example, the production or consumption of one species can be

used to calculate the production or consumption of any of the other species involved in a reaction once you calculate, or are given, the value of the extent of reaction.

EXAMPLE 9.4 Calculation of the Extent of Reaction

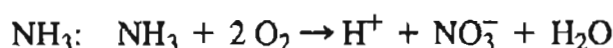
Determine the extent of reaction for the following chemical reaction



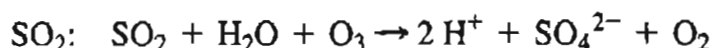
given the following analysis of feed and product:

	<u>Feed</u>	<u>Product</u>
N ₂	100 g	
H ₂	50 g	
NH ₃	5g	90 g

Also, determine the g and g mol of N₂ and H₂ in the product, and the acid rain potential (ARP) of the NH₃. The acid rain potential can be characterized by the number of moles of H⁺ created per number of moles of compound from which the H⁺ are created. For ammonia the reaction considered is



In practice, the potential for acidification is expressed on a mass basis normalized by a reference compound, namely SO₂, for which the reaction considered produces two H⁺



Thus the ARP is calculated as

$$\text{ARP}_i = \frac{\frac{\text{mole H}_i^+}{\text{MW}_i}}{\frac{\text{mole SO}_2}{\text{MW SO}_2}}$$

Solution

The extent of reaction can be calculated by applying Equation (9.3) based on NH₃:

$$n_i = \frac{90 \text{ g NH}_3}{17 \text{ g NH}_3} \left| \frac{1 \text{ g mol NH}_3}{17 \text{ g NH}_3} \right| = 5.294 \text{ g mol NH}_3$$

$$n_{i0} = \frac{5 \text{ g NH}_3}{17 \text{ g NH}_3} \left| \frac{1 \text{ g mole NH}_3}{17 \text{ g NH}_3} \right| = 0.294 \text{ g mol NH}_3$$

$$\xi = \frac{n_i - n_{i0}}{\nu_i} = \frac{(5.294 - 0.204) \text{ g mol NH}_3}{2 \text{ g mol NH}_3/\text{moles reacting}} = 2.50 \text{ moles reacting}$$

Equation (9.4) can be used to determine the g mol of N_2 and H_2 in the products of the reaction

$$N_2: \quad n_{i0} = \frac{100 \text{ g } N_2}{28 \text{ g } N_2} \left| \frac{1 \text{ g mol } N_2}{28 \text{ g } N_2} \right. = 3.57 \text{ g mol } N_2$$

$$n_{N_2} = 3.57 + (-1)(2.5) = 1.07 \text{ g mol } N_2$$

$$m_{N_2} = \frac{1.07 \text{ g mol } N_2}{1 \text{ g mol } N_2} \left| \frac{28 \text{ g } N_2}{1 \text{ g mol } N_2} \right. = 30 \text{ g } N_2$$

$$H_2: \quad n_{i0} = \frac{50 \text{ g } H_2}{2 \text{ g } H_2} \left| \frac{1 \text{ g mol } H_2}{2 \text{ g } H_2} \right. = 25 \text{ g mol } H_2$$

$$n_{H_2} = 25 + (-3)(2.5) = 17.5 \text{ g mol } H_2$$

$$m_{H_2} = \frac{17.5 \text{ g mol } H_2}{1 \text{ g mol } H_2} \left| \frac{2 \text{ g } H_2}{1 \text{ g mol } H_2} \right. = 35 \text{ g } H_2$$

$$\text{The ARP} = (1/17)/(2/64) = 1.88$$

If several independent (refer to Appendix L for the meaning of independent) reactions occur in the reactor, say k of them, ξ can be defined for each reaction, ξ_k . With v_{ki} being the stoichiometric coefficient of species i in the k th reaction, the total number of moles of species i is

$$n_i = n_{i0} + \sum_{k=1}^R v_{ki} \xi_k \quad (9.5)$$

where R is the total number of independent reactions.

To summarize, the important characteristic of the variable ξ defined in Equation (9.3) is that it has the same value for each molecular species involved in a particular reaction. Thus, given the initial mole numbers of all species and a value for ξ (or the change in the number of moles of one species from which the value of ξ can be calculated), you can easily compute all other numbers of moles in the system after the reaction takes place.

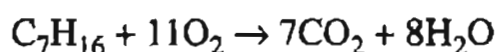
9.2-2 Limiting and Excess Reactants

In industrial reactors you will rarely find exact stoichiometric amounts of materials used. To make a desired reaction take place or to use up a costly reactant, excess reactants are nearly always used. The excess material comes out together with, or perhaps separately from, the product, and sometimes can be used again. The **lim-**

limiting reactant is the species in a chemical reaction that would theoretically run out first (would be completely consumed) if the reaction were to proceed to completion according to the chemical equation—even if the reaction does not proceed to completion! All the other reactants are called **excess reactants**.

$$\% \text{ excess reactant} = 100 \frac{\left\{ \begin{array}{l} \text{amount of the excess reactant fed} - \text{amount of the} \\ \text{excess reactant required to react with the limiting reactant} \end{array} \right\}}{\left\{ \begin{array}{l} \text{amount of the excess reactant required} \\ \text{to react with the limiting reactant} \end{array} \right\}}$$

For example, using the chemical reaction equation in Example 9.2,



if 1 g mol of C_7H_{16} and 12 g mol of O_2 are mixed, C_7H_{16} would be the limiting reactant even if the reaction does not take place. The amount of the **excess reactant** O_2 would be 12 g mol less the 11 g mole needed to react with 1 g mol of C_7H_{16} , or 1 g mol of O_2 . Therefore, if the reaction were to go to completion, the amount of product produced would be controlled by the amount of the limiting reactant.

As a straightforward way of determining the limiting reactant, you can determine the maximum extent of reaction, ξ^{\max} , for each reactant based on the **complete reaction** of the reactant. **The reactant with the smallest maximum extent of reaction is the limiting reactant.** For the example, for 1 g mol of C_7H_{16} plus 12 g mole of O_2 , you calculate

$$\xi^{\max} (\text{based on } \text{O}_2) = \frac{0 \text{ g mol } \text{O}_2 - 12 \text{ g mol } \text{O}_2}{-11 \text{ g mol } \text{O}_2/\text{moles reacting}} = 1.09 \text{ moles reacting}$$

$$\xi^{\max} (\text{based on } \text{C}_7\text{H}_{16}) = \frac{0 \text{ g mol } \text{C}_7\text{H}_{16} - 1 \text{ g mol } \text{C}_7\text{H}_{16}}{-1 \text{ g mol } \text{C}_7\text{H}_{16}/\text{moles reacting}} = 1.00 \text{ moles reacting}$$

Therefore, heptane is the limiting reactant and oxygen is the excess reactant.

Consider the following reaction



If the feed to the reactor contains 1.1 moles of A, 3.2 moles of B, and 2.4 moles of C. The extents of reaction based on complete reaction of A, B, and C are

$$\xi^{\max} (\text{based on A}) = \frac{-1.1 \text{ mol A}}{-1} = 1.1$$

$$\xi^{\max} (\text{based on B}) = \frac{-3.2 \text{ mol B}}{-3} = 1.07$$

$$\xi^{\max} (\text{based on C}) = \frac{-2.4 \text{ mol C}}{-2} = 1.2$$

As a result, B is identified as the limiting reactant in this example while A and C are the excess reactants.

As an alternate to determining the limiting reactant, all you have to do is to calculate the mole ratio(s) of the reactants and compare each ratio with the corresponding ratio of the coefficients of the reactants in the chemical equation thus:

$$\frac{\text{O}_2}{\text{C}_7\text{H}_{16}}: \quad \frac{\text{Ratio in feed}}{\frac{12}{1} = 12} > \frac{\text{Ratio in chemical equation}}{\frac{11}{1} = 11}$$

If more than two reactants are present, you have to use one reactant as the reference substance, calculate the mole ratios of the other reactants in the feed relative to the reference, make pairwise comparisons versus the analogous ratios in the chemical equation, and rank each compound. For example, given the reaction



and that 1.1 moles of A, 3.2 moles of B, and 2.4 moles of C are fed as reactants in the reactor, we choose A as the reference substance and calculate

$$\begin{array}{lll} \frac{B}{A}: & \frac{\text{Ratio in feed}}{\frac{3.2}{1.1} = 2.91} < \frac{\text{Ratio in chemical equation}}{\frac{3}{1} = 3} \\ \frac{C}{A}: & \frac{2.4}{1.1} = 2.18 > \frac{2}{1} = 2 \end{array}$$

We conclude that B is the limiting reactant relative to A, and that A is the limiting reactant relative to C, hence B is the limiting reactant among the set of three reactants. In symbols we have $B < A$, $C > A$ (i.e., $A < C$), so that $B < A < C$.

EXAMPLE 9.5 Calculation of the Limiting and Excess Reactants Given the Mass of Reactants

If you feed 10 grams of N_2 gas and 10 grams of H_2 gas into a reactor:

- What is the maximum number of grams of NH_3 that can be produced?
- What is the limiting reactant?
- What is the excess reactant?

Solution

You are asked to calculate the limiting reactant, and use a chemical reaction equation to calculate the NH_3 produced. At room temperature and pressure no reaction will occur, but you are asked to calculate what would result if the reaction were to occur (as it does under other conditions of temperature and pressure).

Look at Figure E9.5.

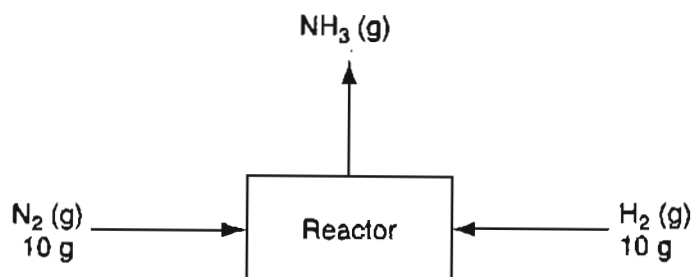


Figure E9.5

Next, write down the chemical equation, and get the molecular weights:

	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightarrow	$2\text{NH}_3(\text{g})$
Given g:	10		10		0
MW:	28		2.016		17.02
Calcd. g mol:	0.357		4.960		0

The next step is to determine the limiting reactant by calculating the maximum extent of reaction based on the complete reaction of N_2 and H_2 .

$$\xi^{\max} (\text{based on } \text{N}_2) = \frac{-0.357 \text{ g mol } \text{N}_2}{-1 \text{ g mol } \text{N}_2/\text{moles reacting}} = 0.357 \text{ moles reacting}$$

$$\xi^{\max} (\text{based on } \text{H}_2) = \frac{-4.960 \text{ g mol } \text{H}_2}{-3 \text{ g mol } \text{H}_2/\text{moles reacting}} = 1.65 \text{ moles reacting}$$

You can conclude that (b) N_2 is the limiting reactant, and that (c) H_2 is the excess reactant. The excess H_2 is $4.960 - 3(0.357) = 3.89 \text{ g mol}$. To answer question (a), the maximum amount of NH_3 that can be produced is based on assuming complete conversion of the limiting reactant

$$\frac{0.357 \text{ g mol } \text{N}_2}{1 \text{ g mol } \text{N}_2} \left| \frac{2 \text{ g mol } \text{NH}_3}{1 \text{ g mol } \text{N}_2} \right| \frac{17.02 \text{ g } \text{NH}_3}{1 \text{ g mol } \text{NH}_3} = 12.2 \text{ g } \text{NH}_3$$

Finally, you should check your answer by working from the answer to the given reactant, or, alternatively, by adding up the mass of the NH_3 and the mass of excess H_2 . What should the sum be?

9.2-3 Conversion and degree of completion

Conversion and degree of completion are terms not as precisely defined as are the extent of reaction and limiting and excess reactant. Rather than cite all the possible usages of these terms, many of which conflict, we shall define them as follows. **Conversion is the fraction of the feed or some key material in the feed that is converted into products.** Conversion is related to the **degree of completion** of a reaction namely the percentage or fraction of the limiting reactant converted into products. The numerator and denominator of the fraction contain the same units so that the fraction conversion is dimensionless. Thus, percent conversion is

$$\% \text{ conversion} = 100 \frac{\text{moles (or mass) of feed (or a compound in the feed) that react}}{\text{moles (or mass) of feed (or a component in the feed) introduced}}$$

For example, for the reaction equation described in Example 9.2, if 14.4 kg of CO_2 are formed in the reaction of 10 kg of C_7H_{16} , you can calculate what percent of the C_7H_{16} is converted to CO_2 (reacts) as follows:

$$\begin{array}{l} \text{C}_7\text{H}_{16} \text{ equivalent} \\ \text{to CO}_2 \text{ in the product} \end{array} \quad \frac{14.4 \text{ kg CO}_2}{44.0 \text{ kg CO}_2} \left| \frac{1 \text{ kg mol CO}_2}{7 \text{ kg mol CO}_2} \right| \frac{1 \text{ kg mol C}_7\text{H}_{16}}{100.1 \text{ kg C}_7\text{H}_{16}} = 0.0468 \text{ kg mol C}_7\text{H}_{16}$$

$$\text{C}_7\text{H}_{16} \text{ in the reactants} \quad \frac{10 \text{ kg C}_7\text{H}_{16}}{100.1 \text{ kg C}_7\text{H}_{16}} = 0.0999 \text{ kg mol C}_7\text{H}_{16}$$

$$\% \text{ conversion} = \frac{0.0468 \text{ mol reacted}}{0.0999 \text{ kg mol fed}} 100 = 46.8\% \text{ of the C}_7\text{H}_{16}$$

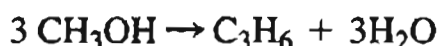
The conversion can also be calculated using the extent of reaction as follows: conversion is equal to the extent of reaction based on CO_2 formation (i.e., the actual extent of reaction) divided by the extent of reaction assuming complete reaction of C_7H_{16} (i.e., the maximum possible extent of reaction).

$$\begin{aligned} \text{conversion} &= \frac{\text{extent of reaction that actually occurs}}{\text{extent of reaction that would occur if complete reaction took place}} \\ &= \frac{\xi}{\xi^{\max}} \end{aligned} \quad (9.5)$$

9.2-4 Selectivity

Selectivity is the ratio of the moles of a particular (usually the desired) product produced to the moles of another (usually undesired or by-product)

product produced in a set of reactions. For example, methanol (CH_3OH) can be converted into ethylene (C_2H_4) or propylene (C_3H_6) by the reactions



Of course, for the process to be economical, the prices of the products have to be significantly greater than the reactants. Examine the data in Figure 9.1 for the concentrations of the products of the reactions. What is the selectivity of C_2H_4 relative to the C_3H_6 at 80% conversion of the CH_3OH ? Proceed upward at 80% conversion to get for $\text{C}_2\text{H}_4 \approx 19$ mole % and for $\text{C}_3\text{H}_6 \approx 8$ mole %. Because the basis for both values is the same, you can compute the selectivity $19/8 \approx 2.4$ mol C_2H_4 per mol C_3H_6 .

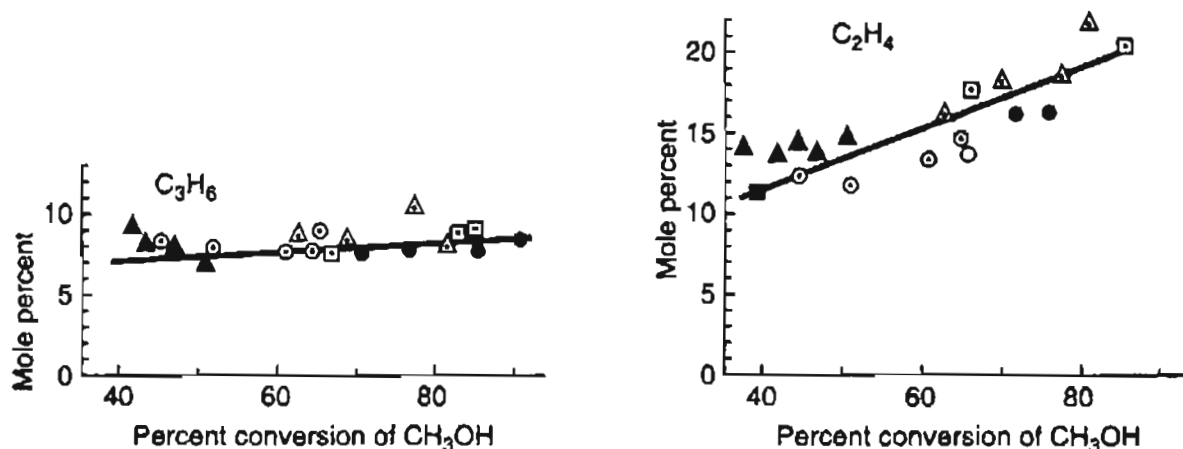


Figure 9.1 Products from the conversion of ethanol.

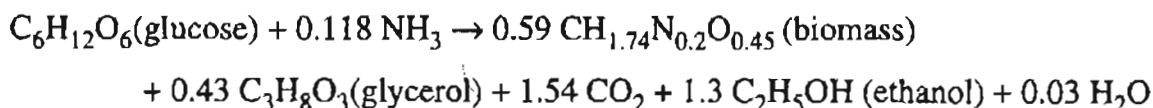
9.2-5 Yield

No universally agreed-upon definitions exist for yield—in fact, quite the contrary. Here are three common ones:

- **yield** (based on feed)—the amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.
- **yield** (based on reactant consumed)—the amount (mass or moles) of desired product obtained divided by amount of the key (frequently the limiting) reactant consumed.
- **yield** (based on theoretical consumption of the limiting reactant)—the amount (mass or moles) of a product obtained divided by the theoretical (expected) amount of the product that would be obtained based on the limiting reactant in the chemical reaction equation(s) if it were completely consumed.

EXAMPLE 9.6 Yields in the Reaction of Glucose to Produce Ethanol

Yeasts are living organisms that consume sugars and produce a variety of products. For example, yeasts are used to convert malt to beer and corn to ethanol. The growth of *S. cerevisiae* (a specific type of yeast) on glucose (a sugar) under anaerobic conditions (in the absence of oxygen) proceeds by the following overall reaction to produce biomass, glycerol, and ethanol



Calculate the theoretical yield of biomass in g of biomass per g of glucose. Also, calculate the yield of ethanol in g of ethanol per g of glucose.

Solution

Basis: 0.59 g mol of biomass

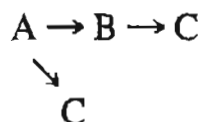
$$\frac{0.59 \text{ g mol biomass}}{1 \text{ g mol glucose}} \left| \frac{23.74 \text{ g biomass}}{1 \text{ g mol biomass}} \right| \frac{1 \text{ g mol glucose}}{180 \text{ g glucose}} = 0.0778 \text{ g biomass/g glucose}$$

$$\frac{1.3 \text{ g mol C}_2\text{H}_5\text{OH}}{1 \text{ g mol glucose}} \left| \frac{46 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ g mol C}_2\text{H}_5\text{OH}} \right| \frac{1 \text{ g mol glucose}}{180 \text{ g glucose}} = 0.332 \text{ g C}_2\text{H}_5\text{OH/g glucose}$$

Why doesn't the actual yield in a reaction equal the theoretical yield predicted from the chemical reaction equation? Several reasons exist:

- impurities among the reactants
- leaks to the environment
- side reactions
- reversible reactions

As an illustration, suppose you have a reaction sequence as follows:



with B being the desired product and C the undesired one. The yield of B according to the first two definitions is the moles (or mass) of B produced divided by the respective moles (or mass) of A fed or consumed. The yield according to the third definition is the moles (or mass) of B divided by the maximum amount of B that could

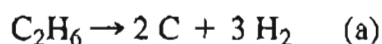
be produced in the reaction sequence. The selectivity of B is the moles of B divided by the moles of C produced.

The terms "yield" and "selectivity" are terms that measure the degree to which a desired reaction proceeds relative to competing alternative (undesirable) reactions. As a designer of equipment you want to maximize production of the desired product and minimize production of the unwanted products. Do you want high or low selectivity? Yield?

EXAMPLE 9.7 Selectivity in the Production of Nanotubes

A carbon nanotube may consist of a single wall tube or a number of concentric tubes. A single wall tube may be produced as unaligned structures or bundles of ropes packed together in an orderly manner. The structure of the nanotubes influences its properties, such as conductance. Some kinds are conductors and some semiconductors.

In nanotechnology, numerous methods (arc-discharge, laser vaporization, chemical vapor deposition, and so on) exist to produce nanotubes. For example, large amounts of single wall carbon nanotubes can be produced by the catalytic decomposition of ethane over Co and Fe catalysts supported on silica



If you collect 3 g mol of H_2 and 0.50 g mol of C_2H_4 , what is the selectivity of C relative to C_2H_4 ?

Solution

Basis: 3 g mol H_2 by Reaction (a)
0.50 g mol C_2H_4 by Reaction (b)

The 0.5 g mol of C_2H_4 corresponds to 0.50 g mol of H_2 produced in Reaction (b). Then the H_2 produced by Reaction (a) was $3 - 0.50 = 2.5$ g mol. Consequently, the nanotubes (the C) produced by Reaction (a) was

$$(2/3)(2.5) = 1.67 \text{ g mol C}$$

The selectivity was

$$1.67/0.50 = 3.33 \text{ g mol C/g mol C}_2\text{H}_4$$

The next example shows you how to calculate all of the terms discussed above in Section 9.2.

EXAMPLE 9.8 Calculation of Various Terms Pertaining to Reactions

Semenov (*Some Problems in Chemical Kinetics and Reactivity*, Princeton Univ. Press (1959), Vol II, pp. 39–42) described some of the chemistry of allyl chlorides. The two reactions of interest for this example are



C_3H_6 is propylene (propene) (MW = 42.08)

$\text{C}_3\text{H}_5\text{Cl}$ is allyl chloride (3-chloropropene) (MW = 76.53)

$\text{C}_3\text{H}_6\text{Cl}_2$ is propylene chloride (1,2—dichloropropane) (MW = 112.99)

The species recovered after the reaction takes place for some time are listed in Table E9.8.

TABLE E9.8

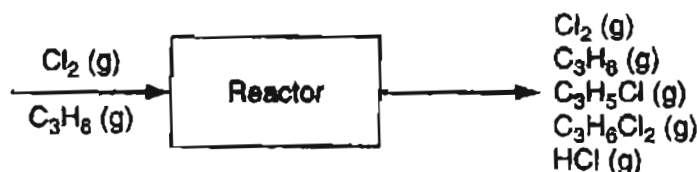
Species	g mol
Cl_2	141.0
C_3H_6	651.0
$\text{C}_3\text{H}_5\text{Cl}$	4.6
$\text{C}_3\text{H}_6\text{Cl}_2$	24.5
HCl	4.6

Based on the product distribution assuming that no allyl chlorides were present in the feed, calculate the following:

- How much Cl_2 and C_3H_6 were fed to the reactor in g mol?
- What was the limiting reactant?
- What was the excess reactant?
- What was the fraction conversion of C_3H_6 to $\text{C}_3\text{H}_5\text{Cl}$?
- What was the selectivity of $\text{C}_3\text{H}_5\text{Cl}$ relative to $\text{C}_3\text{H}_6\text{Cl}_2$?
- What was the yield of $\text{C}_3\text{H}_5\text{Cl}$ expressed in g of $\text{C}_3\text{H}_5\text{Cl}$ to the g of C_3H_6 fed to the reactor?
- What was the extent of reaction of the first and second reactions?
- In the application of green chemistry, you would like to identify classes of chemical reactions that have the potential for process improvement, particularly waste reduction. In this example the waste is HCl (g). The Cl_2 is not considered to be a waste because it is recycled. What is the mole efficiency, i.e., the fraction of an *element* in the entering reactants that emerges in the exiting products, for chlorine?

Solution**Steps 1, 2, 3, and 4**

Examination of the problem statement reveals that the amount of feed is not given, and consequently you must first calculate the g mol fed to the reactor even if the amounts were not asked for. The molecular weights are given. Figure E9.8 illustrates the process as an open-flow system. A batch process could alternatively be used.

**Figure E9.8****Step 5**

A convenient basis is what is given in the product list in Table E9.8.

Steps 7, 8, and 9

Use the chemical equations to calculate the moles of species in the feed.

Reaction (a)

$$\frac{4.6 \text{ g mol C}_3\text{H}_5\text{Cl}}{1 \text{ g mol C}_3\text{H}_5\text{Cl}} \left| \frac{1 \text{ g mol Cl}_2}{1 \text{ g mol C}_3\text{H}_5\text{Cl}} \right| = 4.6 \text{ g mol Cl}_2 \text{ reacts}$$

Reaction (b)

$$\frac{24.5 \text{ g mol C}_3\text{H}_6\text{Cl}_2}{1 \text{ g mol C}_3\text{H}_6\text{Cl}_2} \left| \frac{1 \text{ g mol Cl}_2}{1 \text{ g mol C}_3\text{H}_6\text{Cl}_2} \right| = 24.5 \text{ g mol Cl}_2 \text{ reacts}$$

$$\begin{array}{rcl} \text{Total} & 29.1 \text{ g mol Cl}_2 \text{ reacts} \\ \text{Cl}_2 \text{ in product} & 141.0 \end{array}$$

$$\text{(a)} \quad \text{Total Cl}_2 \text{ fed} \quad 170.1$$

From the chemical equations you can see that if 29.1 g mol Cl₂ reacts by Reactions (a) and (b), 29.1 g mol of C₃H₆ must react. Since 651.0 g mol of C₃H₆ exist in the product,

$$651.0 + 29.1 = 680.1 \text{ g mol of C}_3\text{H}_6$$

were fed to the reactor.

You can check those answers by adding up the respective g mol of Cl, C, and H in the product and comparing the values with that calculated in the feed:

	<u>In product</u>
Cl	$2(141.0) + 1(4.6) + 2(24.5) + 1(4.6) = 340.2$
C	$3(651) + 3(4.6) + 3(24.5) = 2040.3$
H	$6(651) + 5(4.6) + 6(24.5) + 1(4.6) = 4080.6$

	In feed	
Cl	$2(170.1) = 340.2$	OK
C	$3(680.1) = 2040.3$	OK
H	$6(680.1) = 4080.6$	OK

We will not go through detailed steps for the remaining calculations, but simply determine the desired quantities based on the data prepared for Part (a).

(b) and (c) Since both reactions involve the same value of the respective reaction stoichiometric coefficients, both reactions will have the same limiting and excess reactants

$$\xi^{\max} \text{ (based on } C_3H_6) = \frac{-680.1 \text{ g mol } C_3H_6}{-1 \text{ g mol } C_3H_6/\text{moles reacting}} = 680.1 \text{ moles reacting}$$

$$\xi^{\max} \text{ (based on } Cl_2) = \frac{-170.1 \text{ g mole } Cl_2}{-1 \text{ g mol } Cl_2/\text{moles reacting}} = 170.1 \text{ moles reacting}$$

Thus, C_3H_6 was the excess reactant and Cl_2 the limiting reactant.

(d) The fraction conversion of C_3H_6 to C_3H_5Cl was

$$\frac{4.6 \text{ g mol } C_3H_6 \text{ that reacted}}{680.1 \text{ g mol } C_3H_6 \text{ fed}} = 6.76 \times 10^{-3}$$

(e) The selectivity was

$$\frac{4.6 \text{ g mol } C_3H_5Cl}{24.5 \text{ g mol } C_3H_6Cl_2} = 0.19 \frac{\text{g mol } C_3H_5Cl}{\text{g mol } C_3H_6Cl_2}$$

(f) The yield was

$$\frac{(76.53)(4.6) \text{ g } C_3H_5Cl}{(42.08)(680.1) \text{ g } C_3H_6} = 0.012 \frac{\text{g } C_3H_5Cl}{\text{g } C_3H_6}$$

(g) Because C_3H_5Cl is produced only by the first reaction, the extent of reaction of the first reaction is

$$\xi_1 = \frac{n_i - n_{io}}{\nu_i} = \frac{4.6 - 0}{1} = 4.6$$

Because $C_3H_6Cl_2$ is produced only by the second reaction, the extent of reaction of the second reaction is

$$\xi_2 = \frac{n_i - n_{io}}{\nu_i} = \frac{24.5 - 0}{1} = 24.5$$

(h) Mole efficiency in the waste:

Entering Cl: $(170.1)(2) = 340.2 \text{ g mol}$

Exiting Cl in HCl: 4.6 g mol

$$\frac{\text{mole of chlorine in waste}}{\text{mole of chlorine entering}} = \frac{4.6}{340.2} = 0.0135$$

Mole efficiency of the product $= 1 - 0.0135 = 0.987$

It would be difficult to find a better reaction pathway to obtain the indicated products. Of course, the processing of the HCl (g) must be considered.

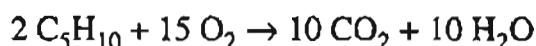
SELF-ASSESSMENT TEST

Questions

1. What is the symbol used to denote the extent of reaction?
2. What is a limiting reactant?
3. What is an excess reactant?
4. How do you calculate the extent of reaction from experimental data?

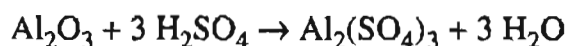
Problems

1. For the reaction in which stoichiometric quantities of the reactants are fed



and the reaction goes to completion, what is the maximum extent of reaction based on C_5H_{10} ? On O_2 ? Are the respective values different or the same? Explain the result.

2. Calcium oxide (CaO) is formed by decomposing limestone (pure CaCO_3). In one kiln the reaction goes to 70% completion.
 - a. What is the composition of the solid product withdrawn from the kiln?
 - b. What is the yield in terms of pounds of CO_2 produced per pound of limestone fed into the process?
3. Aluminum sulfate can be made by reacting crushed bauxite ore with sulfuric acid, according to the following chemical equation:



The bauxite ore contains 55.4% by weight of aluminum oxide, the remainder being impurities. The sulfuric acid solution contains 77.7% pure sulfuric acid, the remainder being water.

To produce crude aluminum sulfate containing 1798 lb of pure aluminum sulfate, 1080 lb of bauxite ore and 2510 lb of sulfuric acid solution are reacted.

- Identify the excess reactant.
- What percentage of the excess reactant was consumed?
- What was the degree of completion of the reaction?

4. Two well-known gas phase reactions take place in the dehydration of ethane:



Given the product distribution measured in the gas phase reaction of C_2H_6 as follows

C_2H_6	27%
C_2H_4	33%
H_2	13%
CH_4	27%

- What species was the limiting reactant?
- What species was the excess reactant?
- What was the conversion of C_2H_6 to CH_4 ?
- What was the degree of completion of the reaction?
- What was the selectivity of C_2H_4 relative to CH_4 ?
- What was the yield of C_2H_4 expressed in kg mol of C_2H_4 produced per kg mol of C_2H_6 ?
- What was the extent of reaction of C_2H_6 ?

Thought Problem

- OSHA requires the use of a breathing apparatus when working in or around tanks containing traces of solvents. While demolishing an old tank, a contractor purchased several cylinders of compressed air, painted gray. After two days he found that he needed more cylinders, and sent a truck for another cylinder. The driver returned with a black cylinder. None of the workers, including the man in charge of the breathing apparatus, noticed the change or, if they did, attached any importance to it. When the new cylinder was brought into use, a welder's face piece caught fire. Fortunately, he pulled it off at once and was not injured.

What would be the most likely cause of this accident?

Discussion Problem

- On November 1, 1986, a fire at a Sandoz storehouse near Basel, Switzerland, resulted in a substantial number of insecticides, pesticides, dyes, and other raw and intermediate materials being introduced into the Rhine River via runoff of about 15,000 m³ water used in fighting the fire. From Basel to the North Sea where the Rhine discharges is about 1200

km. The table lists some of the compounds discharged into the river along with the LC50 value (the concentration that will kill 50% of rainbow trout).

Compound	Estimated discharge (kg)	Estimated concentration near discharge point ($\mu\text{g/L}$)	LC50 ($\mu\text{g/L}$)
Disulfostor (I)	3000-9000	600	6000
Thiometon (I)	1200-4000	500	8000
Ethoxyethyl mercury hydroxide (P)	18-200	12	3 to 1000
DNOC (P)	600-2000	100-430	66 to 1250
Endosulfan (P)	20-60	3-13	1.4

I = insecticide; P = pesticide

What were the probable consequences of the discharge along the river to the fish, biota, drinking water, and benthic organisms? Note that the Rhine has several dams to provide water for navigation. What would the concentration of these compounds be as a function of time at various towns downstream of Basel?

Looking Back

In this chapter we explained how the chemical reaction equation can be used to calculate quantitative relations among reactants and products. We also defined a number of terms used by engineers in making calculations involving chemical reactions.

GLOSSARY OF NEW WORDS

Conversion The fraction of the feed or some *key* material in the feed that is converted into products.

Degree of completion The percent or fraction of the limiting reactant converted into products.

Excess reactant All reactants other than limiting reactant.

Extent of reaction $\xi = \frac{n_i - n_{i0}}{\nu_i}$

where n_i is the number of moles of species i present in the system after the reaction occurs, n_{i0} is the number of moles of species i present in the system when the reaction starts, and ν_i is the stoichiometric coefficient for species i in the chemical equation.

Limiting reactant The species in a chemical reaction that would theoretically run out first (would be completely consumed) if the reaction were to proceed to

completion according to the chemical equation—even if the reaction did not take place.

Selectivity The ratio of the moles of a particular (usually the desired) product produced to the moles of another (usually undesired or by-product) product produced in a set of reactions.

Stoichiometric coefficient Tells the relative amounts of moles of chemical species that react and are produced in a chemical reaction.

Stoichiometric ratio Mole ratio obtained by using the coefficients of the species in the chemical equation including both reactants and products.

Stoichiometry Concerns calculations about the moles and masses of reactants and products involved in a chemical reaction(s).

Yield (based on feed) The amount (mass or moles) of a desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.

Yield (based on reactant consumed) The amount (mass or moles) of a desired product obtained divided by the amount of the key (frequently the limiting) reactant consumed.

Yield (based on theoretical consumption of the limiting reactant) The amount (mass or moles) of a product obtained divided by the theoretical (expected) amount of the product that would be obtained based on the limiting reactant in the chemical reaction equation(s) being completely consumed.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent.

Atkins, P. W. *Physical Chemistry*, 6th ed., Oxford University Press, Oxford, UK (1998).

Atkins, P. W., and L. L. Jones. *Chemistry, Molecules, Matter, and Change*. Freeman, New York (1997).

Brady, J. E. *Liftoff! Chemistry*. Ehrlich Multimedia, John Wiley, New York (1996).

Kotz, J. C., and P. Treichel. *Chemistry and Chemical Reactivity*. Saunders, Fort Worth, TX (1996).

Peckham, G. D. "The Extent of Reaction—Some Nuts and Bolts," *J. Chem. Educ.*, **78**, 508–510 (2001).

Web Sites

<http://dbhs.wvusd.k12.ca.us/Stoichiometry>

<http://www.chem.ualberta.ca/courses/plambeck/p101.new>

<http://science.widener.edu/svb/pset/limiting>

<http://www.gsu.edu/~mstjrh/stoichiometry>

<http://www.shsu.edu/web/schools/SHSU/chm/tchastee/14/modules>

PROBLEMS

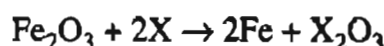


- (a) How many grams of barium chloride will be required to react with 5.00 g of sodium sulfate?
- (b) How many grams of barium chloride are required for the precipitation of 5.00 g of barium sulfate?
- (c) How many grams of barium chloride are needed to produce 5.00 g of sodium chloride?
- (d) How many grams of sodium sulfate are necessary for the precipitation of 5.00 g of barium chloride?
- (e) How many grams of sodium sulfate have been added to barium chloride if 5.00 g of barium sulfate is precipitated?
- (f) How many pounds of sodium sulfate are equivalent to 5.00 lb of sodium chloride?
- (g) How many pounds of barium sulfate are precipitated by 5.00 lb of barium chloride?
- (h) How many pounds of barium sulfate are precipitated by 5.00 lb of sodium sulfate?
- (i) How many pounds of barium sulfate are equivalent to 5.00 lb of sodium chloride?



- (a) How many grams of silver nitrate will be required to react with 5.00 g of sodium chloride?
- (b) How many grams of silver nitrate are required for the precipitation of 5.00 g of silver chloride?
- (c) How many grams of silver nitrate are equivalent to 5.00 g of sodium nitrate?
- (d) How many grams of sodium chloride are necessary for the precipitation of the silver of 5.00 g of silver nitrate?
- (e) How many grams of sodium chloride have been added to silver nitrate if 5.00 g of silver chloride is precipitated?
- (f) How many pounds of sodium chloride are equivalent to 5.00 lb of sodium nitrate?
- (g) How many pounds of silver chloride are precipitated by 5.00 lb of silver nitrate?
- (h) How many pounds of silver chloride are precipitated by 5.00 lb of sodium chloride?
- (i) How many pounds of silver chloride are equivalent to 5.00 lb of silver nitrate?

- *9.3 A plant makes liquid CO_2 by treating dolomitic limestone with commercial sulfuric acid. The dolomite analyzes 68.0% CaCO_3 , 30.0% MgCO_3 , and 2.0% SiO_2 ; the acid is 94% H_2SO_4 and 6% H_2O . Calculate:
- Pounds of CO_2 produced per ton dolomite treated.
 - Pounds of acid used per ton of dolomite treated.
- **9.4 Balance the following reactions (find the values of a_i):
- $a_1\text{As}_2\text{S}_3 + a_2\text{H}_2\text{O} + a_3\text{HNO}_3 \rightarrow a_4\text{NO} + a_5\text{H}_3\text{AsO}_4 + a_6\text{H}_2\text{SO}_4$
 - $a_1\text{KClO}_3 + a_2\text{HCl} \rightarrow a_3\text{KCl} + a_4\text{ClO}_2 + a_5\text{Cl}_2 + a_6\text{H}_2\text{O}$
- *9.5 The following reaction was carried out:



It was found that 79.847 g of Fe_2O_3 reacted with "X" to form 55.847 g of Fe and 50.982 g X_2O_3 . Identify the element X.

- **9.6 A combustion device was used to determine the empirical formula of a compound containing only carbon, hydrogen, and oxygen. A 0.6349 g sample of the unknown produced 1.603 g of CO_2 and 0.2810 g of H_2O . Determine the empirical formula of the compound.
- *9.7 A hydrate is a crystalline compound in which the ions are attached to one or more water molecules. We can dry these compounds by heating them to get rid of the water. You have a 10.407-g sample of hydrated barium iodide. The sample is heated to drive off the water. The dry sample has a mass of 9.520 g. What is the mole ratio between barium iodide, BaI_2 , and water, H_2O ? What is the formula of the hydrate?
- *9.8 The formula for vitamin C is as follows:
How many pounds of this compound are contained in 2 g mol?

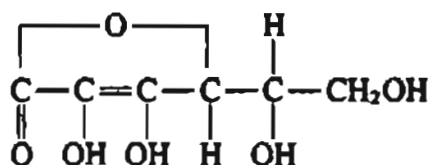


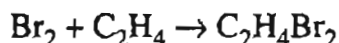
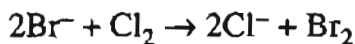
Figure P9.8

- *9.9 Sulfuric acid can be manufactured by the contact process according to the following reactions:
- $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
 - $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$
 - $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

You are asked as part of the preliminary design of a sulfuric acid plant with a production capacity of 2000 tons/day of 66° Be (Baumé) (93.2% H_2SO_4 by weight) to calculate the following:

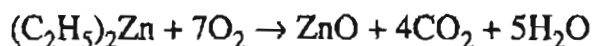
- How many tons of pure sulfur are required per day to run this plant?
- How many tons of oxygen are required per day?
- How many tons of water are required per day for reaction (3)?

- *9.10 Seawater contains 65 ppm of bromine in the form of bromides. In the Ethyl-Dow recovery process, 0.27 lb of 98% sulfuric acid is added per ton of water, together with the theoretical Cl_2 for oxidation; finally, ethylene (C_2H_4) is united with the bromine to form $\text{C}_2\text{H}_4\text{Br}_2$. Assuming complete recovery and using a basis of 1 lb of bromine, find the weights of the 98% sulfuric acid, chlorine, seawater, and ethane dibromide involved.



- *9.11 Acidic residue in paper from the manufacturing process causes paper based on wood pulp to age and deteriorate. To neutralize the paper, a vapor-phase treatment must employ a compound that would be volatile enough to permeate the fibrous structure of paper within a mass of books but that would have a chemistry that could be manipulated to yield a mildly basic and essentially non-volatile compound. George Kelly and John Williams successfully attained this objective in 1976 by designing a mass-deacidification process employing gaseous diethyl zinc (DEZ).

At room temperature, DEZ is colorless liquid. It boils at 117°C . When it is combined with oxygen, a highly exothermic reaction takes place:



Because liquid DEZ ignites spontaneously when exposed to air, a primary consideration in its use is the exclusion of air. In one case a fire caused by DEZ ruined the neutralization center.

Is the equation shown balanced? If not, balance it. How many kg of DEZ must react to form 1.5 kg of ZnO? If 20 cm^3 of water are formed on reaction, and the reaction was complete, how many grams of DEZ reacted?

- *9.12

BID EVALUATION

TO: J. Coadwell DEPT: Water Waste Water DATE: 9-29

BID INVITATION: 0374-AV

REQUISITION: 135949 COMMODITY: Ferrous Sulfate

DEPARTMENT EVALUATION COMMENTS

It is recommended that the bid from VWR of \$83,766.25 for 475 tons of Ferrous Sulfate Heptahydrate be accepted as they were the low bidder for this product as delivered. It is further recommended that we maintain the option of having this product delivered either by rail in a standard carload of 50 tons or by the alternate method by rail in piggy-back truck trailers.

What would another company have to bid to match the VWR bid if the bid they submitted was for ferrous sulfate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$)? For ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$)?

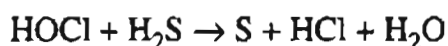
- *9.13 Three criteria must be met if a fire is to occur: (1) There must be fuel present; (2) there must be an oxidizer present; and (3) there must be an ignition source. For most fuels, combustion takes place only in the gas phase. For example, gasoline does not burn as a liquid. However, when gasoline is vaporized, it burns readily.

A minimum concentration of fuel in air exists that can be ignited. If the fuel concentration is less than this lower flammable limit (LFL) concentration, ignition will not occur. The LFL can be expressed as a volume percent, which is equal to the mole percent under conditions at which the LFL is measured (atmospheric pressure and 25°C). There is also a minimum oxygen concentration required for ignition of any fuel. It is closely related to the LFL and can be calculated from the LFL. The minimum oxygen concentration required for ignition can be estimated by multiplying the LFL concentration by the ratio of the number of moles of oxygen required for complete combustion to the number of moles of fuel being burned.

Above the LFL, the amount of energy required for ignition is quite small. For example, a spark can easily ignite most flammable mixtures. There is also a fuel concentration called the upper flammable limit (UFL) above which the fuel-air mixture cannot be ignited. Fuel-air mixtures in the flammable concentration region between the LFL and the UFL can be ignited. Both the LFL and the UFL have been measured for most of the common flammable gases and volatile liquids. The LFL is usually the more important of the flammability concentrations because if a fuel is present in the atmosphere in concentrations above the UFL, it will certainly be present within the flammable concentration region at some location. LFL concentrations for many materials can be found in the NFPA Standard 325M, "Properties of Flammable Liquids," published by the National Fire Protection Association.

Estimate the minimum permissible oxygen concentration for *n*-butane. The LFL concentration for *n*-butane is 1.9 mole percent. This problem was originally based on a problem in the text *Chemical Process Safety: Fundamentals with Applications*, by D.A. Crowl and J.F. Louvar, published by Prentice Hall, Englewood Cliffs, NJ, and has been adapted from Problem 10 of the AIChE publication, *Safety, Health, and Loss Prevention in Chemical Processes* by J.R. Welker and C. Springer, New York (1990).

- *9.14 Odors in wastewater are caused chiefly by the products of the anaerobic reduction of organic nitrogen and sulfur-containing compounds. Hydrogen sulfide is a major component of wastewater odors; however, this chemical is by no means the only odor producer since serious odors can also result in its absence. Air oxidation can be used to remove odors, but chlorine is the preferred treatment because it not only destroys H_2S and other odorous compounds but it also retards the bacteria that cause the compounds in the first place. As a specific example, HOCl reacts with H_2S as follows in low pH solutions



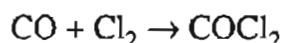
If the actual plant practice calls for 100% excess HOCl (to make sure of the destruction of the H_2S because of the reaction of HOCl with other substances), how much HOCl (5% solution) must be added to 1L of a solution containing 50 ppm H_2S ?

- *9.15** In a paper mill, soda ash (Na_2CO_3) can be added directly in the causticizing process to form, on reaction with calcium hydroxide, caustic soda (NaOH) for pulping. The overall reaction is $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NaOH} + \text{CaCO}_3$. Soda ash also may have potential in the on-site production of precipitated calcium carbonate, which is used as a paper filler. The chloride in soda ash (which causes corrosion of equipment) is 40 times less than in regular grade caustic soda (NaOH) which can also be used, hence the quality of soda ash is better for pulp mills. However, a major impediment to switching to soda ash is the need for excess causticization capacity, generally not available at older mills.

Severe competition exists between soda ash and caustic soda produced by electrolysis. Average caustic soda prices are about \$265 per metric ton FOB (free on board, i.e., without charges for delivery to or loading on carrier) while soda ash prices are about \$130/metric ton FOB.

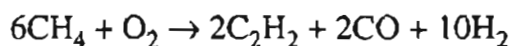
To what value would caustic soda prices have to drop in order to meet the price of \$130/metric ton based on an equivalent amount of NaOH ?

- *9.16** A hazardous waste incinerator has been burning a certain mass of dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$) per hour, and the HCl produced was neutralized with soda ash (Na_2CO_3). If the incinerator switches to burning an equal mass of mixed tetrachlorobiphenyls ($\text{C}_{12}\text{H}_6\text{Cl}_4$), by what factor will the consumption of soda ash be increased?
- *9.17** Phosgene gas is probably most famous for being the first toxic gas used offensively in World War I, but it is also used extensively in the chemical processing of a wide variety of materials. Phosgene can be made by the catalytic reaction between CO and chlorine gas in the presence of a carbon catalyst. The chemical reaction is

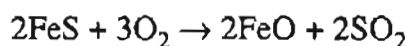


Suppose that you have measured the reaction products from a given reactor and found that they contained 3.00 lb moles of chlorine, 10.00 lb moles of phosgene, and 7.00 lb moles CO . Calculate the extent of reaction, and using the value calculated, determine the initial amounts of CO and Cl_2 that were used in the reaction.

- *9.18** In the reaction in which 135 moles of methane and 45.0 moles of oxygen are fed into a reactor, if the reaction goes to completion, calculate the extent of reaction.



- *9.19** FeS can be roasted in O_2 to form FeO .



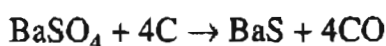
If the slag (solid product) contains 80% FeO and 20% FeS , and the exit gas is 100% SO_2 , determine the extent of reaction and the initial number of moles of FeS . Use 100 g or 100 lb as the basis.

- *9.20** Aluminum sulfate is used in water treatment and in many chemical processes. It can be made by reacting crushed bauxite (aluminum ore) with 77.7 weight percent sulfuric acid. The bauxite ore contains 55.4 weight percent aluminum oxide, the remainder being impurities. To produce crude aluminum sulfate containing 2000 lb of pure aluminum sulfate, 1080 lb of bauxite and 2510 lb of sulfuric acid solution (77.7 percent acid) are used.

- (a) Identify the excess reactant.
 (b) What percentage of the excess reactant was used?
 (c) What was the degree of completion of the reaction?
- *9.21** A barytes composed of 100 percent BaSO_4 is fused with carbon in the form of coke containing 6 percent ash (which is infusible). The composition of the fusion mass is

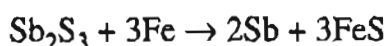
BaSO_4	11.1%
BaS	72.8
C	13.9
Ash	<u>2.2</u>
	100.0%

Reaction:



Find the excess reactant, the percentage of the excess reactant, and the degree of completion of the reaction.

- *9.22** Read Problem 9.17 again. Suppose that you have measured the reaction products from a given reactor and found that they contained 3.00 kg of chlorine, 10.00 kg of phosgene, and 7.00 kg of CO. Calculate the following:
- (a) The percent excess reactant used.
 (b) The percentage conversion of the limiting reactant.
 (c) The kg mol of phosgene formed per kg mol of total reactants fed to the reactor.
- **9.23** Antimony is obtained by heating pulverized stibnite (Sb_2S_3) with scrap iron and drawing off the molten antimony from the bottom of the reaction vessel.



Suppose that 0.600 kg of stibnite and 0.250 kg of iron turnings are heated together to give 0.200 kg of Sb metal. Determine:

- (a) The limiting reactant
 (b) The percentage of excess reactant
 (c) The degree of completion (fraction)
 (d) The percent conversion based on Sb_2S_3
 (e) The yield in kg Sb produced/kg Sb_2S_3 fed to the reactor.
- *9.24** The specific activity of an enzyme is defined in terms of the amount of solution catalyzed under a given set of conditions divided by the product of the time interval for the reaction times the amount of protein in the sample:

$$\text{specific activity} = \frac{\mu \text{ mol of solution converted}}{(\text{time interval in minutes})(\text{mg protein in the sample})}$$

A 0.10 mL sample of pure β -galactosidase (β -g) solution that contains 1.00 mg of protein per L, hydrolyzed 0.10 mmol of o-nitrophenyl galactoside (o-n) in 5 minutes. Calculate the specific activity of the β -g.

- *9.25** One method of synthesizing the aspirin substitute, acetaminophen, involves a three-step procedure as outlined in Figure P9.25. First, p-nitrophenol is catalytically hydro-

generated in the presence of aqueous hydrochloric acid to the acid chloride salt of *p*-aminophenol with a 86.9% degree of completion. Next the salt is neutralized to obtain *p*-aminophenol with a 0.95 fractional conversion.

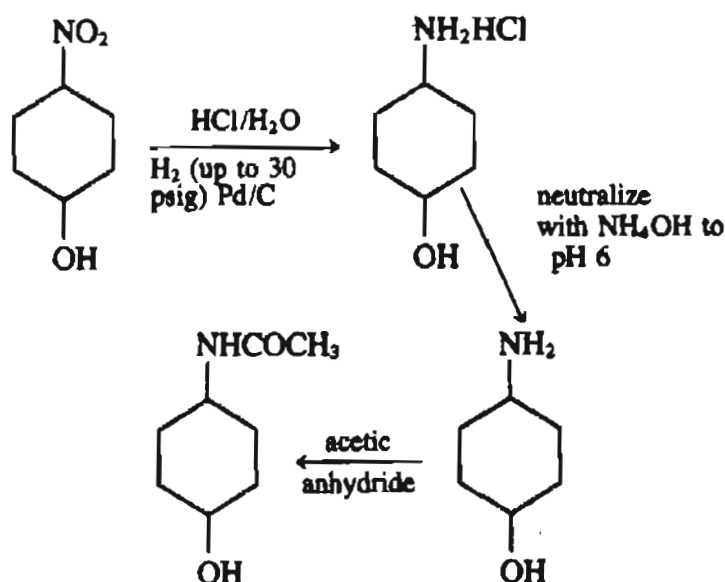
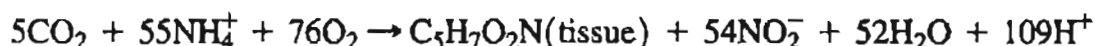


Figure P9.25

Finally, the *p*-aminophenol is acetylated by reacting with acetic anhydride, resulting in a yield of 3 kg mol of acetaminophen per 4 kg mol. What is the overall conversion fraction of *p*-nitrophenol to acetaminophen?

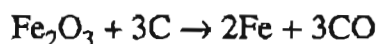
- *9.26 The most economic method of sewage wastewater treatment is bacterial digestion. As an intermediate step in the conversion of organic nitrogen to nitrates, it is reported that the *Nitrosomonas* bacteria cells metabolize ammonium compounds into cell tissue and expel nitrite as a by-product by the following overall reaction:



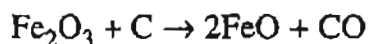
If 20,000 kg of wastewater containing 5% ammonium ions by weight flows through a septic tank inoculated with the bacteria, how many kilograms of cell tissue are produced, provided that 95% of the NH_4^+ is consumed?

✓**9.27
1.121

One can view the blast furnace from a simple viewpoint as a process in which the principal reaction is



but some other undesired side reactions occur, mainly



After mixing 600.0 lb of carbon (coke) with 1.00 ton of pure iron oxide, Fe_2O_3 , the process produces 1200.0 lb of pure iron, 183 lb of FeO, and 85.0 lb of Fe_2O_3 . Calculate the following items:

- (a) The percentage of excess carbon furnished, based on the principal reaction

- (b) The percentage conversion of Fe_2O_3 to Fe
- (c) The pounds of carbon used up and the pounds of CO produced per ton of Fe_2O_3 charged
- (d) What is the selectivity in this process (of Fe with respect to FeO)?

****9.28**

A common method used in manufacturing sodium hypochlorite bleach is by the reaction



Chlorine gas is bubbled through an aqueous solution of sodium hydroxide, after which the desired product is separated from the sodium chloride (a by-product of the reaction). A water-NaOH solution that contains 1145 lb of pure NaOH is reacted with 851 lb of gaseous chlorine. The NaOCl formed weighs 618 lb.

- (a) What was the limiting reactant?
- (b) What was the percentage excess of the excess reactant used?
- (c) What is the degree of completion of the reaction, expressed as the moles of NaOCl formed to the moles of NaOCl that would have formed if the reaction had gone to completion?
- (d) What is the yield of NaOCl per amount of chlorine used (on a weight basis)?
- (e) What was the extent of reaction?

✓9.29**

In a process for the manufacture of chlorine by direct oxidation of HCl with air over a catalyst to form Cl_2 and H_2O (only), the exit product is composed of HCl (4.4%), Cl_2 (19.8%), H_2O (19.8%), O_2 (4.0%), and N_2 (52.0%). What was

- (a) the limiting reactant?
- (b) the percent excess reactant?
- (c) the degree of completion of the reaction?
- (d) the extent of reaction?

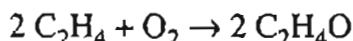
****9.30**

A well known reaction to generate hydrogen from steam is the so called water gas shift reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. If the gaseous feed to a reactor consists of 30 moles of CO per hour, 12 moles of CO_2 per hour, and 35 moles of steam per hour at 800°C , and 18 moles of H_2 are produced per hour, calculate

- (a) the limiting reactant.
- (b) the excess reactant.
- (c) the fraction conversion of steam to H_2 .
- (d) the degree of completion of the reaction.
- (e) the kg of H_2 yielded per kg of steam fed.
- (f) the moles of CO_2 produced by the reaction per mole of CO fed.
- (g) the extent of reaction.

***9.31**

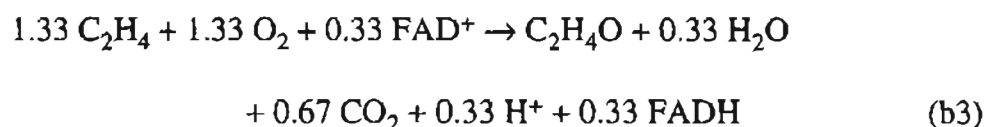
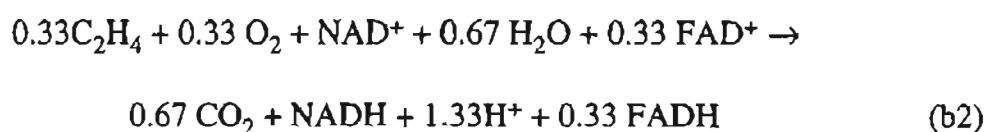
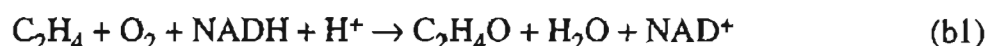
The overall yield of a product on a substrate in some bioreactions is the absolute value of the production rate divided by the rate of consumption of the feed in the substrate (the liquid containing the cells, nutrients, etc.) The overall chemical reaction for the oxidation of ethylene (C_2H_4) to epoxide ($\text{C}_2\text{H}_4\text{O}$) is



(a)

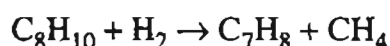
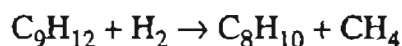
Calculate the theoretical yield (100% conversion C_2H_4) of C_2H_4O in mol per mol for Reaction (a).

The biochemical pathway for the production of epoxide is quite complex. Co-factor regeneration is required which is assumed to originate by partial further oxidation of the formed epoxide. Thus, the amount of ethylene consumed to produce 1 mole of epoxide is larger than that required by Reaction (a). The following two reactions, (b1) and (b2), when summed approximate the overall pathway



Calculate the theoretical yield for Reaction (b3) of the epoxide.

- *9.32 In the production of m-xylene (C_8H_{10}) from mesitylene (C_9H_{12}) over a catalyst, some of the xylene reacts to form toluene (C_7H_8):



The second reaction is undesirable because m-xylene sells for \$0.65/lb whereas toluene sells for \$0.22/lb.

The CH_4 is recycled in the plant. One pound of catalyst is degraded per 500 lb of C_7H_8 produced, and the spent catalyst has to be disposed of in a landfill that handles low-level toxic waste at a cost of \$25/lb. If the overall selectivity of C_8H_{10} to C_7H_8 is changed from 0.7 mole of xylene produced/mole of toluene produced to 0.8 by changing the residence time in the reactor, what is the gain or loss in \$/100 lb of mesitylene reacted.

CHAPTER 10

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

10.1 Species Material Balances	261
10.2 Element Material Balances	278
10.3 Material Balances Involving Combustion	283

Your objectives in studying this chapter are to be able to:

1. Carry out a degree of freedom analysis for processes involving chemical reaction(s).
2. Formulate and solve material balances using (a) species balances and (b) element balances.
3. Decide when element balances can be used as material balances.
4. Determine if a set of chemical reaction equations is a minimal set.
5. Understand how the extent of reaction is determined for a process, and how to apply it in material balance problems.
6. Understand the meanings of stack gas, flue gas, Orsat analysis, dry basis, wet basis, theoretical air (oxygen) and excess air (oxygen), and employ these concepts in combustion problems.

Why are we devoting a whole chapter to discussing material balances for systems with reaction? The heart of many plants is the reactor in which products and by-products are manufactured. To be able to design and operate a reactor economically and safely you have to be able to make valid material balances for the reactor (and associated equipment) often in real time. Of course, computer programs can make the calculations for you, but you have to put the right information into them, and

... to calculate is not in itself to analyze.

Edgar Allen Poe in "Murders in the Rue Morgue"

Looking Ahead

This chapter discusses material balances for reacting systems. We begin by discussing material balances based on chemical species, and then examine material balances made using chemical elements. The third section focuses on combustion processes.

10.1 Species Material Balances

10.1-1 Processes Involving a Single Reaction

Do you recall from Section 6.5 that the material balance for a species must be augmented to include generation and consumption terms when chemical reactions occur in a process? In terms of moles of species i :

$$\left\{ \begin{array}{l} \text{moles of} \\ i \text{ at } t_2 \\ \text{in the} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{l} \text{moles of} \\ i \text{ at } t_1 \\ \text{in the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{l} \text{moles of } i \\ \text{entering} \\ \text{the system} \\ \text{between } t_2 \text{ and } t_1 \end{array} \right\} - \left\{ \begin{array}{l} \text{moles of } i \\ \text{leaving} \\ \text{the system} \\ \text{between } t_2 \text{ and } t_1 \end{array} \right\} + \left\{ \begin{array}{l} \text{moles of } i \\ \text{generated} \\ \text{by reaction} \\ \text{between } t_2 \text{ and } t_1 \end{array} \right\} - \left\{ \begin{array}{l} \text{moles of } i \\ \text{consumed} \\ \text{by reaction} \\ \text{between } t_2 \text{ and } t_1 \end{array} \right\} \quad (10.1)$$

Note that we have written Equation (10.1) in moles rather than mass because the generation and consumption terms are more conveniently represented in moles.

How do you include the variables corresponding to the generation and consumption terms in Equation (10.1) and still maintain the independence of the species material balances? You have to be sure to avoid redundant equations as well as excess variables. Fortunately, you do not have to add an additional variable to account for the generation or consumption of species i for each species present in the system if you make use of the extent of reaction that was discussed in Chapter 9.

To make the idea clear, consider the well-known reaction of N_2 and H_2 to form NH_3 . Figure 10.1 presents the process as an open, steady-state system operating for 1 min so that the accumulation terms are zero on the lefthand side of the equal sign in Equation (10.1). The data in Figure 10.1 are in g mol.

Using Equation (10.1) you can calculate via a value in g mol for the generation or consumption, as the case may be, for each of the three species involved in the reaction:

$$\text{NH}_3 \text{ (generation):} \quad 6 - 0 = 6 \text{ g mol}$$

$$\text{H}_2 \text{ (consumption):} \quad 9 - 18 = -9 \text{ g mol}$$

$$\text{N}_2 \text{ (consumption):} \quad 12 - 15 = -3 \text{ g mol}$$

As you know from the stoichiometry of the chemical reaction equation

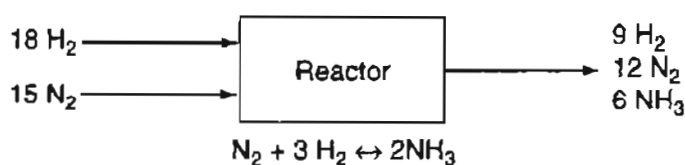


Figure 10.1. A reactor to produce NH_3 .

the respective three generation and consumption terms are related by the reaction equation. Given the value for the generation of NH_3 , you can calculate the values for the consumption of H_2 and N_2 using the reaction equation. Thus, the generation and consumption terms are not independent, and you cannot specify more than one of the values without introducing a redundant or inconsistent specification. In general, if you specify the value for the generation or consumption of one of the N species in a reaction, you are able to calculate the values of the $N-1$ other species from the chemical reaction equation.

Here is where the extent of reaction ξ becomes useful. Recall that for an open system

$$\xi = \frac{n_i^{\text{out}} - n_i^{\text{in}}}{\nu_i} \quad i = 1, \dots, N \quad (10.2)$$

where ν_i is the stoichiometric coefficient of species i in the reaction equation (refer to Section 9.2). For the NH_3 reaction

$$\nu_{\text{NH}_3} = 2$$

$$\nu_{\text{H}_2} = -3$$

$$\nu_{\text{N}_2} = -1$$

and the extent of reaction can be calculated via any species:

$$\xi = \frac{n_{\text{NH}_3}^{\text{out}} - n_{\text{NH}_3}^{\text{in}}}{\nu_{\text{NH}_3}} = \frac{6 - 0}{2} = 3$$

$$\xi = \frac{n_{\text{H}_2}^{\text{out}} - n_{\text{H}_2}^{\text{in}}}{\nu_{\text{H}_2}} = \frac{9 - 18}{-3} = 3$$

$$\xi = \frac{n_{\text{N}_2}^{\text{out}} - n_{\text{N}_2}^{\text{in}}}{\nu_{\text{N}_2}} = \frac{12 - 15}{-1} = 3$$

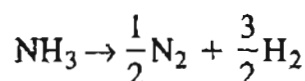
You can conclude for the case of a single chemical reaction that the specification of the extent of reaction provides the one independent quantity that accounts for all of the values of the generation and consumption terms for the various species in the respective implementations of Equation (10.1). The three species balances corresponding to the process in Figure 10.1 are

Component	Out	In	=	Generation or Consumption
i	n_i^{out}	$-n_i^{in}$	=	$v_i \xi$
NH ₃ :	6	-0	=	2 (3) = 6
H ₂ :	9	-18	=	-3 (3) = -9
N ₂ :	12	-15	=	-1 (3) = -3

The term $v_i \xi$ corresponds to the moles of i generated or consumed.

Frequently Asked Questions

1. Does it make any difference how the chemical reaction equation is written? No. While the value for the extent of reaction may change, the relative values for the generation and consumption of species will remain the same. For example, write the ammonia reaction as a decomposition of ammonia



Calculate ξ for the process in Figure 10.1. Based on NH₃

$$\xi = \frac{6 - 0}{-1} = -6$$

and the material balance is

$$6 - 0 = (-1)(-6) = 6$$

If you repeat the above calculation for H₂, what result do you get?

2. Does it make any difference if the process in Figure 10.1 is transformed into a closed (batch) system? No. You can treat the process as a closed, unsteady-state system by changing your viewpoint as explained in Chapter 6. For a closed, unsteady-state system the flows in and out would be zero, and Equation (10.1) would become

$$\frac{n_i^{\text{final}} - n_i^{\text{initial}}}{v_i} = \xi \quad (10.3)$$

For convenience we usually treat a reactor as an open system, and use Equation (10.2) even though the reaction may occur in a batch reactor. You get the same results for ξ from either viewpoint.

In making a degree-of-freedom analysis, you can write *one independent material balance* equation for each species present in the system. If Equation (10.2) is applied to each species that reacts, the resulting set of equations will all contain the extent of reaction ξ . For the species that do not react, $\xi = 0$. In terms of the total molar flow in and the total molar flow out

$$F^{out} = \sum_{i=1}^S n_i^{out}$$

$$F^{in} = \sum_{i=1}^S n_i^{in}$$

where S is the total number of species in the system (n_i may be zero for some species). The material balance for the total molar flow is

$$F^{out} = F^{in} + \xi \sum_{i=1}^S \nu_i \quad (10.4)$$

Baldy's Law: Some of it plus the rest of it is all of it.

Paul Dickson

Equation (10.4) is not an independent equation, but can be substituted for one of the species balances. Only S independent equations can be written for the system. Does Equation (10.4) apply to a closed system? No. For a closed system you would sum the respective n_i in Equation (10.3) over the final and initial moles in the system.

If you add one more unknown, ξ , in the set of independent species equations, you will, of course, have to add one more piece of information in the problem statement in order to be able to solve a problem. For example, you might be given the value of the fraction conversion f of the limiting reactant; ξ is related to f by

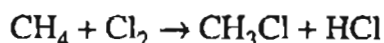
$$\xi = \frac{(-f)n_{\text{limiting reactant}}^{in}}{\nu_{\text{limiting reactant}}} \quad (10.5)$$

Consequently, you can calculate the value of ξ from the fraction conversion (or vice versa) plus information identifying the limiting reactant. In other cases you are given sufficient information about the moles of a species entering and leaving the process so that ξ can be calculated directly.

Now let's look at some examples.

EXAMPLE 10.1 Reaction in Which the Fraction Conversion Is Specified

The chlorination of methane occurs by the following reaction



You are asked to determine the product composition if the conversion of the limiting reactant is 67%, and the feed composition in mole % is given as: 40% CH_4 , 50% Cl_2 , and 10% N_2 .

Solution**Steps 1, 2, 3, and 4**

Assume the reactor is an open, steady-state process. Figure E10.1 is a sketch of the process with the known information placed on it.

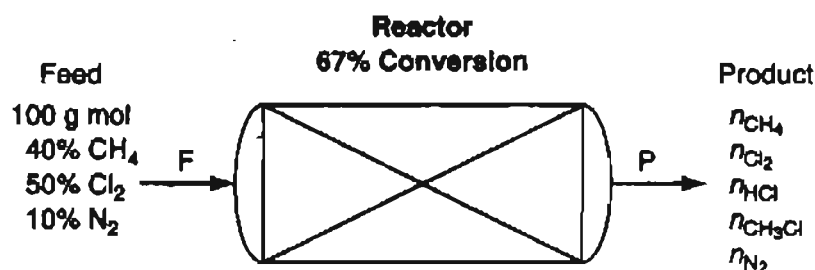


Figure E10.1

Step 5

Select as a basis 100 g mol feed

Step 4

You have to determine the limiting reactant if you are to make use of the information about the 67% conversion. By comparing the maximum extent of reaction (refer to Chapter 9) for each reactant, you can identify the limiting reactant.

$$\xi^{\max}(\text{CH}_4) = \frac{-n_{\text{CH}_4}^{\text{in}}}{\nu_{\text{CH}_4}} = \frac{-40}{(-1)} = 40$$

$$\xi^{\max}(\text{Cl}_2) = \frac{-n_{\text{Cl}_2}^{\text{in}}}{\nu_{\text{Cl}_2}} = \frac{-50}{(-1)} = 50$$

Therefore, CH_4 is the limiting reactant. You can now calculate the extent of reaction using the specified conversion rate and Equation (10.5).

$$\xi = \frac{-f n_{lr}^{\text{in}}}{\nu_{lr}} = \frac{(-0.67)(40)}{-1} = 26.8 \text{ g moles reacting}$$

Steps 6 and 7

The next step is to carry out a degree-of-freedom analysis

Number of variables: 11

$$n_{\text{CH}_4}^{\text{in}}, n_{\text{Cl}_2}^{\text{in}}, n_{\text{N}_2}^{\text{in}}, n_{\text{CH}_4}^{\text{out}}, n_{\text{Cl}_2}^{\text{out}}, n_{\text{HCl}}^{\text{out}}, n_{\text{CH}_3\text{Cl}}^{\text{out}}, n_{\text{N}_2}^{\text{out}}, F, P, \xi$$

Number of equations: 11

Basis: $F = 100$

Species material balances: 5



Specifications: 3

Two of $\{x_{\text{CH}_4}^{\text{in}}, x_{\text{Cl}_2}^{\text{in}}, x_{\text{N}_2}^{\text{in}}\}$ and f (used to calculate ξ)

Implicit equations: 2

$$\sum n_i^{\text{out}} = P \text{ and } \sum n_i^{\text{in}} = F$$

The degrees of freedom are zero.

Steps 8 and 9

The species material balances (in moles) using Equation (10.2) give a direct solution for each species in the product:

$$n_{\text{CH}_4}^{\text{out}} = 40 - 1(26.8) = 13.2$$

$$n_{\text{Cl}_2}^{\text{out}} = 50 - 1(26.8) = 23.2$$

$$n_{\text{CH}_3\text{Cl}}^{\text{out}} = 0 + 1(26.8) = 26.8$$

$$n_{\text{HCl}}^{\text{out}} = 0 + 1(26.8) = 26.8$$

$$n_{\text{N}_2}^{\text{out}} = 10 - 0(26.8) = \underline{10.0}$$

$$100.0 = P$$

Therefore, the composition of the product stream is: 13.2% CH_4 , 23.2% Cl_2 , 26.8% CH_3Cl , 26.8% HCl , and 10% N_2 because the total number of product moles is conveniently 100 g mol. There are 100 g mol of products because there are 100 g mol of feed and the chemical reaction equation results in the same number of moles for reactants as products by coincidence.

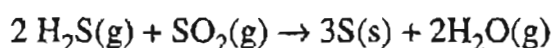
Step 10

The fact that the overall mole balance equation is satisfied is not a consistency check for this problem.

EXAMPLE 10.2 A Reaction in Which the Fraction Conversion Is To Be Calculated

Mercaptans, hydrogen sulfide, and other sulfur compounds are removed from natural gas by various so-called "sweetening processes" that make available otherwise useless "sour" gas. As you know H_2S is toxic in very small quantities and is quite corrosive to process equipment.

A proposed process to remove H_2S is by reaction with SO_2 :



In a test of the process, a gas stream containing 20% H_2S and 80% CH_4 was combined with a stream of pure SO_2 . The process produced 5000 lb of $\text{S}(\text{s})$, and in the product gas the ratio of SO_2 to H_2S was equal to 3, and the ratio of H_2O to H_2S was 10. You are asked to determine the fractional conversion of the limiting reactant, and the feed rates of the H_2S and SO_2 streams.

Solution

This problem in a sense is the reverse of Example 10.1. Instead of being given the fraction conversion, you are asked to calculate the value. What this change means is that ξ will have to be calculated from the material balance equations, and then f from Equation (10.5).

Steps 1, 2, 3, and 4

Figure E10.2 is a diagram of the process with the known data inserted.

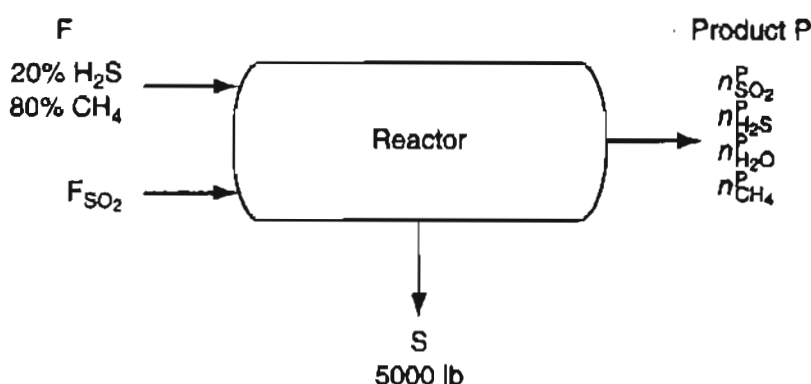


Figure E10.2

Step 5

The obvious basis is 5000 lb S (156.3 lb mol S)

Steps 6 and 7

The next step is to carry out a degree-of-freedom analysis.

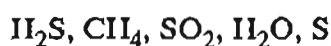
Number of variables: 11

$$n_{\text{H}_2\text{S}}^F, n_{\text{CH}_4}^F, F_{\text{SO}_2}, n_{\text{SO}_2}^P, n_{\text{H}_2\text{S}}^P, n_{\text{H}_2\text{O}}^P, n_{\text{CH}_4}^P, \xi, F, P, S$$

Number of equations: 11

Basis: $S = 5000 \text{ lb}$ (156.3 lb mol)

Species material balances: 5



Specifications: 4 (3 independent)

$$x_{\text{H}_2\text{S}}^F = 0.20 \text{ or } x_{\text{CH}_4}^F = 0.80, (n_{\text{SO}_2}^P/n_{\text{H}_2\text{S}}^P) = 3, (n_{\text{H}_2\text{O}}^P/n_{\text{H}_2\text{S}}^P) = 10$$

Implicit equations: 2

$$\sum n_i^P = P \quad \sum n_i^F = F \text{ (redundant if you use both specifications in } F)$$

The degrees of freedom are zero, and the problem is exactly specified.

Step 8

The species balances in pound moles after introduction of most of the specifications are:

$$\text{S: } 156.3 = 0 + 3\xi \quad (\text{a})$$

$$\text{H}_2\text{S: } n_{\text{H}_2\text{S}}^P = 0.20F - 2\xi \quad (\text{b})$$

$$\text{SO}_2: n_{\text{SO}_2}^P = F_{\text{SO}_2} - 1\xi \quad (\text{c})$$

$$\text{H}_2\text{O: } n_{\text{H}_2\text{O}}^P = 0 + 2\xi \quad (\text{d})$$

$$\text{CH}_4: n_{\text{CH}_4}^P = 0.80F + 0(\xi) \quad (\text{e})$$

The remaining specifications are

$$n_{\text{SO}_2}^P = 3n_{\text{H}_2\text{S}}^P \quad (\text{f})$$

$$n_{\text{H}_2\text{O}}^P = 10n_{\text{H}_2\text{S}}^P \quad (\text{g})$$

Equations (a) through (g) comprise seven independent equations and seven unknowns.

Step 9

If you solve the equations without using a computer, you should start by calculating ξ from Equation (a)

$$\xi = \frac{156.3 \text{ mol}}{3} = 52.1 \text{ mol rxn}$$

Then Equation (d) gives

$$n_{\text{H}_2\text{O}}^P = 2(52.1) = 104.2 \text{ lb mol H}_2\text{O}$$

Next, Equation (g) gives

$$n_{\text{H}_2\text{S}}^P = \frac{1}{10} n_{\text{H}_2\text{O}}^P = 10.4 \text{ lb mol H}_2\text{S}$$

and Equation (f) gives

$$n_{\text{SO}_2}^P = 3(10.4) = 31.2 \text{ lb mol SO}_2$$

If you solve the rest of the equations in the order (b), (c), and (e), you find

$$F = 573 \text{ lb mol}$$

$$F_{\text{SO}_2} = 83.3 \text{ lb mol}$$

$$n_{\text{CH}_4}^F = 458 \text{ lb mol}$$

Finally, you can identify H_2S as the limiting reactant because the molar ratio of SO_2 to H_2S in the product gas (3/1) is greater than the molar ratio in the chemical reaction equation (2/1). The fractional conversion from Equation (10.5) is the consumption of H_2S divided by the total feed of H_2S

$$f = \frac{-(-2)\xi}{0.2F} = \frac{(2)(52.1)}{(0.2)(573)} = 0.91$$

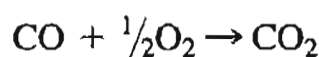
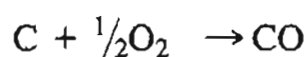
Step 10

Because of the coincidence of the equality of moles of reactants and products for this particular reaction, you cannot use the overall mole balance for this process as a consistency check.

10.1-2 Processes Involving Multiple Reactions

In practice reaction systems rarely involve just a single reaction. A primary reaction (e.g., the desired reaction) can occur, but there are invariably additional or side reactions. To extend the concept of the extent of reaction to processes involving multiple reactions, the question is do you just include a ξ for every reaction. The answer is no. You should **include in the species material balances only the ξ_i associated with a (nonunique) set of independent chemical reactions called the minimal* set of reaction equations.** What this term means is the smallest set of chemical reactions equations that can be assembled that includes *all* of the species involved in the process. Analogous to a set of independent linear algebraic equations, you can form any other reaction equation by a linear combination of the reaction equations contained in the minimal set.

For example, look at the following set of reaction equations:



*Sometimes called the *maximal set*.

By inspection you can see that if you subtract the second equation from the first one, you obtain the third equation. Only two of the three equations are independent, hence the minimal set is comprised of any two of the three equations. Refer to Appendix L1 for information about using a computer to determine if a set of chemical reaction equations comprise an independent set.

With these ideas in mind, we can state that for open, steady-state processes with multiple reactions, Equation (10.1) in moles becomes for component i

$$n_i^{\text{out}} = n_i^{\text{in}} + \sum_{j=1}^R \nu_{ij} \xi_j \quad (10.6)$$

where

ν_{ij} is the stoichiometric coefficient of species i in reaction j in the minimal set.

ξ_j is the extent of reaction for the j th reaction in the minimal set.

R is the number of independent chemical reaction equations (the size of the minimal set).

An equation analogous to Equation (10.6) can be written for a closed, unsteady-state system. Try it. If you get stuck, look at Example 10.4.

The total moles, N , exiting a reactor are

$$N = \sum_{i=1}^S n_i^{\text{out}} = \sum_{i=1}^S n_i^{\text{in}} + \sum_{i=1}^S \sum_{j=1}^R \nu_{ij} \xi_j \quad (10.7)$$

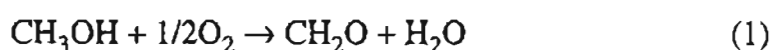
where S is the number of species in the system. What Equation (10.7) means in words is add up the stoichiometric coefficients for each independent reaction, multiply the sum by ξ for that reaction, and then sum the resulting products for each reaction to get N .

Frequently Asked Question

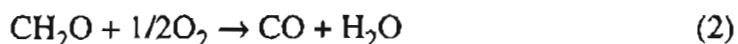
Do you have to know all of the reaction equations in a process in order to get the value for the number of independent reactions? No. All you need is a list of the species involved in the reactions. Refer to Appendix L1 for the procedure.

EXAMPLE 10.3 Material Balances for a Process in Which Two Simultaneous Reactions Occur

Formaldehyde (CH_2O) is produced industrially by the catalytic oxidation of methanol (CH_3OH) according to the following reaction:



Unfortunately, under the conditions used to produce formaldehyde at a profitable rate, a significant portion of the formaldehyde reacts with oxygen to produce CO and H₂O, that is,



Assume that methanol and twice the stoichiometric amount of air needed for complete conversion of the CH₃OH to the desired products (CH₂O and H₂O) are fed to the reactor. Also assume that 90% conversion of the methanol results, and that a 75% yield of formaldehyde occurs based on the theoretical production of CH₂O by Reaction 1. Determine the composition of the product gas leaving the reactor.

Solution

Steps 1, 2, 3, and 4

Figure E10.3 is a sketch of the process with y_i indicating the mole fraction of the respective components in P (a gas).

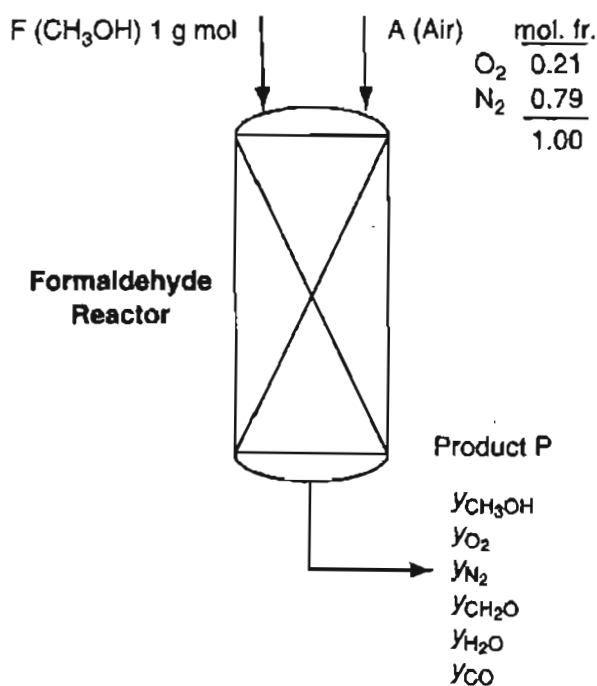


Figure E10.3

Step 5

Basis: 1g mol F

Step 4

You can use the specified conversion of methanol and yield of formaldehyde to determine the extents of reaction for the two reactions. Let ξ_1 represent the extent

of reaction for the first reaction, and ξ_2 represent the extent of reaction for the second reaction. The limiting reactant is CH_3OH .

Use the fraction conversion, Equation (10.5): $\xi_1 = \frac{-0.90}{-1}(1) = 0.9 \text{ g moles}$ reacting

The yield is related to ξ_i as follows

$$\text{By reaction 1: } n_{\text{CH}_2\text{O}}^{\text{out},1} = n_{\text{CH}_2\text{O}}^{\text{in},1} + 1(\xi_1) = 0 + \xi_1 = \xi_1$$

$$\text{By reaction 2: } n_{\text{CH}_2\text{O}}^{\text{out},2} = n_{\text{CH}_2\text{O}}^{\text{in},2} - 1(\xi_2) = n_{\text{CH}_2\text{O}}^{\text{out},1} - \xi_2 = \xi_1 - \xi_2$$

$$\text{The yield is } \frac{n_{\text{CH}_2\text{O}}^{\text{out},2}}{F} = \frac{\xi_1 - \xi_2}{1} = 0.75$$

$$\xi_2 = 0.15 \text{ g moles reacting}$$

You should next calculate the amount of air (A) that enters the process. The entering oxygen is twice the required oxygen based on Reaction 1, namely

$$n_{\text{O}_2}^A = 2\left(\frac{1}{2}F\right) = 2\left(\frac{1}{2}\right)(1.00) = 1.00 \text{ g mol}$$

$$A = \frac{n_{\text{O}_2}^A}{0.21} = \frac{1.00}{0.21} = 4.76 \text{ g mol}$$

$$n_{\text{N}_2}^A = 4.76 - 1.00 = 3.76 \text{ g mol}$$

Steps 6 and 7

The degree-of-freedom analysis is

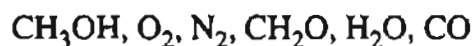
Number of variables: 11

$$F, A, P, y_{\text{CH}_3\text{OH}}^P, y_{\text{O}_2}^P, y_{\text{N}_2}^P, y_{\text{CH}_2\text{O}}^P, y_{\text{H}_2\text{O}}^P, y_{\text{CO}}^P, \xi_1, \xi_2$$

Number of equations: 11

$$\text{Basis: } F = 1 \text{ g mol}$$

Species material balances: 6



Calculated values in Step 4: 3

$$A, \xi_1, \xi_2$$

Implicit equation: 1

$$\sum y_i^P = 1$$

Step 8

Because the variables in Figure E10.3 are y_i^P and not n_i^P , direct use of y_i^P in the material balances will involve the nonlinear terms $y_i^P P$. Consequently, to avoid this situation, let us first calculate P using Equation (10.7):

$$\begin{aligned} P &= \sum_{i=1}^S n_i^{in} + \sum_{i=1}^S \sum_{j=1}^R v_{ij} \xi_j \\ &= 1 + 4.76 + \sum_{i=1}^6 \sum_{j=1}^2 v_{ij} \xi_j \\ &= 5.76 + [(-1) + (-1/2) + (1) + 0 + (1) + 0] 0.9 \\ &\quad + [0 + (-1/2) + (-1) + 0 + (1) + (1)] 0.15 = 6.28 \text{ g mol} \end{aligned}$$

The material balances after entering the values calculated in Step 4 are:

$$\begin{aligned} n_{\text{CH}_3\text{OH}}^{\text{out}} &= y_{\text{CH}_3\text{OH}} (6.28) = 1 - (0.9) + 0 = 0.10 \\ n_{\text{O}_2}^{\text{out}} &= y_{\text{O}_2} (6.28) = 1.0 - (1/2)(0.9) - (1/2)(0.15) = 0.475 \\ n_{\text{CH}_2\text{O}}^{\text{out}} &= y_{\text{CH}_2\text{O}} (6.28) = 0 + 1(0.9) - 1(0.15) = 0.75 \\ n_{\text{H}_2\text{O}}^{\text{out}} &= y_{\text{H}_2\text{O}} (6.28) = 0 + 1(0.9) + 1(0.15) = 1.05 \\ n_{\text{CO}}^{\text{out}} &= y_{\text{CO}} (6.28) = 0 + 0 + 1(0.15) = 0.15 \\ n_{\text{N}_2}^{\text{out}} &= y_{\text{N}_2} (6.28) = 3.76 - 0 - 0 = 3.76 \end{aligned}$$

Step 10

You can check the value of P by adding all of the n_i^{out} above.

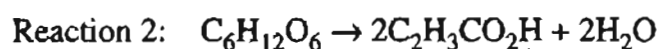
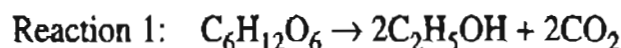
Step 9

The six equations can be solved for the y_i :

$$\begin{aligned} y_{\text{CH}_3\text{OH}} &= 1.6\%, & y_{\text{O}_2} &= 7.6\%, & y_{\text{N}_2} &= 59.8\%, \\ y_{\text{CH}_2\text{O}} &= 11.9\%, & y_{\text{H}_2\text{O}} &= 16.7\%, & y_{\text{CO}} &= 2.4\%. \end{aligned}$$

EXAMPLE 10.4 Analysis of a Bioreactor

A bioreactor is a vessel in which biological conversion is carried out involving enzymes, microorganisms, and/or animal and plant cells. In the anaerobic fermentation of grain, the yeast *Saccharomyces cerevisiae* digests glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) from plants to form the products ethanol ($\text{C}_2\text{H}_5\text{OH}$) and propenoic acid ($\text{C}_2\text{H}_3\text{CO}_2\text{H}$) by the following overall reactions:



In a batch process, a tank is charged with 4000 kg of a 12% solution of glucose in water. After fermentation, 120 kg of CO_2 are produced and 90 kg of unreacted glucose remains in the broth. What are the weight (mass) percents of ethanol and propenoic acid in the broth at the end of the fermentation process? Assume that none of the glucose is assimilated into the bacteria.

Solution

We will view this process as an unsteady-state process in a closed system. For component i , Equation (10.1) becomes analogous to Equation (10.6)

$$n_i^{\text{final}} = n_i^{\text{initial}} + \sum_{j=1}^R v_{ij} \xi_j$$

The bioorganisms do not have to be included in the solution of the problem.

Steps 1, 2, 3, and 4

Figure E10.4 is a sketch of the process.

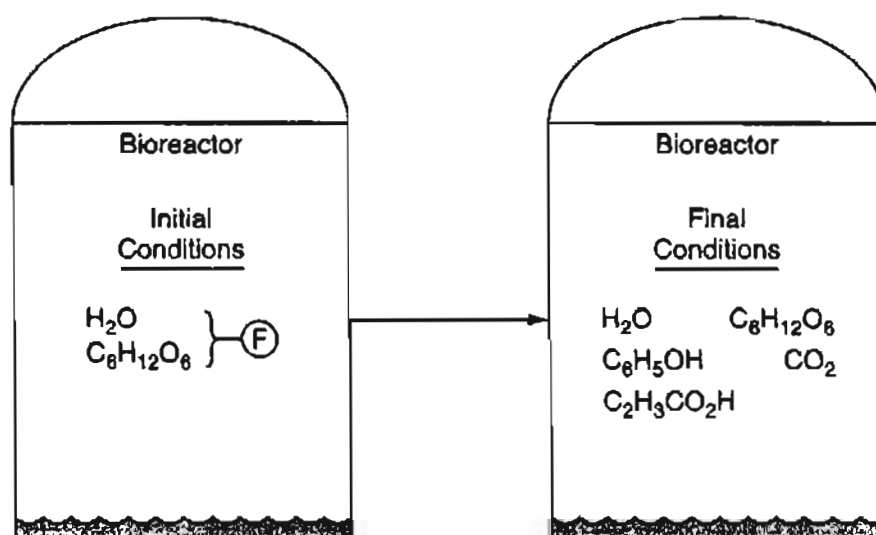


Figure E10.4

Step 5

Basis: 4000 kg F

Step 4

You should convert the 4000 kg into moles of H_2O and $\text{C}_6\text{H}_{12}\text{O}_6$.

$$n_{\text{H}_2\text{O}}^{\text{Initial}} = \frac{4000(0.88)}{18.02} = 195.3$$

$$n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Initial}} = \frac{4000(0.12)}{180.1} = 2.665$$

Steps 6 and 7

The degree-of-freedom analysis is as follows:

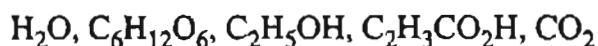
Number of variables: 9

$$n_{\text{H}_2\text{O}}^{\text{Initial}}, n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Initial}}, n_{\text{H}_2\text{O}}^{\text{Final}}, n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Final}}, n_{\text{C}_2\text{H}_5\text{OH}}^{\text{Final}}, n_{\text{C}_2\text{H}_3\text{CO}_2\text{H}}^{\text{Final}}, n_{\text{CO}_2}^{\text{Final}}, \xi_1, \xi_2$$

Number of equations: 9

Basis: 4000 kg of initial solution (equivalent to initial moles of H_2O plus moles of sucrose)

Species material balances: 5



Specifications: 4 (3 independent)

$$n_{\text{H}_2\text{O}}^{\text{Initial}} = 195.3 \text{ or } n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Initial}} = 2.665 \text{ (one is independent, the sum is } F \text{ in mol)}$$

$$n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Final}} = \frac{90}{180.1} = 0.500 \quad n_{\text{CO}_2}^{\text{Final}} = \frac{120}{44} = 2.727$$

The degrees of freedom are zero.

Step 8

The material balance equations, after introducing the known values for the variables, are:

$$\text{H}_2\text{O}: \quad n_{\text{H}_2\text{O}}^{\text{Final}} = 195.3 + (0)\xi_1 + (2)\xi_2 \quad (\text{a})$$

$$\text{C}_6\text{H}_{12}\text{O}_6: \quad 0.500 = 2.665 + (-1)\xi_1 + (-1)\xi_2 \quad (\text{b})$$

$$\text{C}_2\text{H}_5\text{OH}: \quad n_{\text{C}_2\text{H}_5\text{OH}}^{\text{Final}} = 0 + 2\xi_1 + (0)\xi_2 \quad (\text{c})$$

$$\text{C}_2\text{H}_3\text{CO}_2\text{H}: \quad n_{\text{C}_2\text{H}_3\text{CO}_2\text{H}}^{\text{Final}} = 0 + (0)\xi_1 + (2)\xi_2 \quad (\text{d})$$

$$\text{CO}_2: \quad 2.727 = 0 + (2)\xi_1 + (0)\xi_2 \quad (\text{e})$$

If you do not use a computer to solve the equations, the sequence you should use to solve them would be

(e) (b) simultaneously, and then solve, (a), (c), and (d) in order.

Step 9

The solution of Equations (a) – (e) is

$$\xi_1 = 1.364 \text{ kg moles reacting}$$

$$\xi_2 = 0.801 \text{ kg moles reacting}$$

<u>Species</u>	<u>Results</u>	<u>Conversion to mass percent</u>		
	<u>kg kmol</u>	<u>MW</u>	<u>kg</u>	<u>Mass %</u>
H ₂ O	196.9	18.01	3546.1	88.7
C ₂ H ₅ OH	2.728	46.05	125.6	3.1
C ₂ H ₃ CO ₂ H	1.602	72.03	115.4	2.9
CO ₂	2.277	44.0	120.0	3.0
C ₆ H ₁₂ O ₆	0.500	180.1	90.1	2.3
			<u>3997</u>	<u>1.00</u>

Step 10

The total mass of 3977 kg is close enough to 4000 kg of feed to validate the results of the calculations.

SELF-ASSESSMENT TEST

Questions

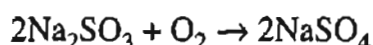
- Answer the following statements true (T) or false (F).
 - If a chemical reaction occurs, the total masses entering and leaving the system for an open, steady-state process are equal.
 - In the combustion of carbon, all of the moles of carbon that enter an open, steady-state process exit from the process.
 - The number of moles of a chemical compound entering a steady-state process in which a reaction occurs with that compound can never equal the number of moles of the same compound leaving the process.
- List the circumstances for a steady-state process in which the number of moles entering the system equals the number of moles leaving the system.
- If Equation (10.2) is to be applied to a compound, what information must be given about the stoichiometry involved and/or the extent of reaction?
- Equation (10.2) can be applied to processes in which a reaction and also no reaction occurs. For what types of balances does the simple relation "the input equals the output" hold for *open, steady-state processes* (no accumulation)? Fill in the blanks yes or no.

Type of balance	Without chemical reaction	With chemical reaction
Total balances		
Total mass	[]	[]
Total moles	[]	[]
Component balances		
Mass of a pure compound	[]	[]
Moles of a pure compound	[]	[]
Mass of an atomic species	[]	[]
Moles of an atomic species	[]	[]

5. Explain how the extent of reaction is related to the fraction conversion of the limiting reactant.

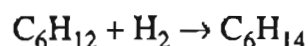
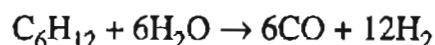
Problems

- Hydrofluoric acid (HF) can be manufactured by treating calcium fluoride (CaF_2) with sulfuric acid (H_2SO_4). A sample of fluorospar (the raw material) contains 75% by weight CaF_2 and 25% inert (nonreacting) materials. The pure sulfuric acid used in the process is in 30% excess of that theoretically required. Most of the manufactured HF leaves the reaction chamber as a gas, but a solid cake that contains 5% of all the HF formed, plus CaSO_4 , inerts, and unreacted sulfuric acid is also removed from the reaction chamber. Assume complete conversion of the CaF_2 occurs. How many kilograms of *cake* are produced per 100 kg of fluorospar charged to the process?
- Corrosion of pipes in boilers by oxygen can be alleviated through the use of sodium sulfite. Sodium sulfite removes oxygen from boiler feedwater by the following reaction:



How many pounds of sodium sulfite are theoretically required (for complete reaction) to remove the oxygen from 8,330,000 lb of water (10^6 gal) containing 10.0 parts per million (ppm) of dissolved oxygen and at the same time maintain a 35% excess of sodium sulfite?

- Consider a continuous, steady-state process in which the following reactions take place:



In the process 250 moles of C_6H_{12} and 800 moles of H_2O are fed into the reactor each hour. The yield of H_2 is 40.0% and the selectivity of H_2 relative to C_6H_{14} is 12.0. Calculate the molar flow rates of all five components in the output stream.

Discussion Problems

- A scheme has been proposed for use on the moon to generate oxygen. The idea is to pass an electric current through molten silica to release oxygen at the anode. Silicon is produced at the cathode. What problems do you anticipate might occur with the proposed

process if the silica contains contaminants such as iron? Will the process have to take place at a high temperature? Where might the electric energy come from?

2. A liquid-emulsion membrane process that offers the promise of cleaning up waste streams contaminated with metals was demonstrated by the Copper Co. on June 1. The process was reported to recover 92–98% of the copper from solutions containing 320–1400 ppm of copper at a feed rate of up to 4 L/min. The emulsion consists of globules of aqueous solution surrounded by an organic phase that contains a reagent selective for copper. The metal loaded emulsion is removed by flotation, and the copper collected by a high voltage electrical field.

Does this process involve a reaction(s)? How would you involve the extent of reaction in making material balances on the process?

10.2 Element Material Balances

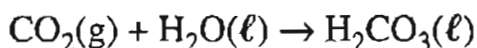
In Section 10.1, you learned how to use species mole balances in solving problems involving reacting systems. Equation (10.1), which included terms for the generation and consumption of each reacting species, was the basic equation from which the other equations were derived.

As you know, elements in a process are conserved, and consequently you can apply Equation (10.1) to the elements in a process. Because elements are not generated or consumed, the generation and consumption terms in Equation (10.1) can be ignored. Why not use element balances to solve material balance problems rather than species balances?

*How wonderful that we have met with a paradox.
Now we have some hope of making progress.*

Niels Bohr

You can, but you must first make sure that the element balances are independent. Species balances are always independent. Here is an illustration of the issue. Carbon dioxide is absorbed in water in the process shown in Figure 10.2. The reaction is



Three unknowns exist: W , F , and P , and the process involves three elements: C, H, and O. It would appear that you can use the three element balances (in moles)

$$\text{C: } W(0) + F(1) = 0.05P(1)$$

$$\text{H: } W(2) + F(0) = [0.05(2) + 0.95(2)]P = 2P$$

$$\text{O: } W(1) + F(2) = [0.05(3) + 0.95(1)]P = 1.10P$$

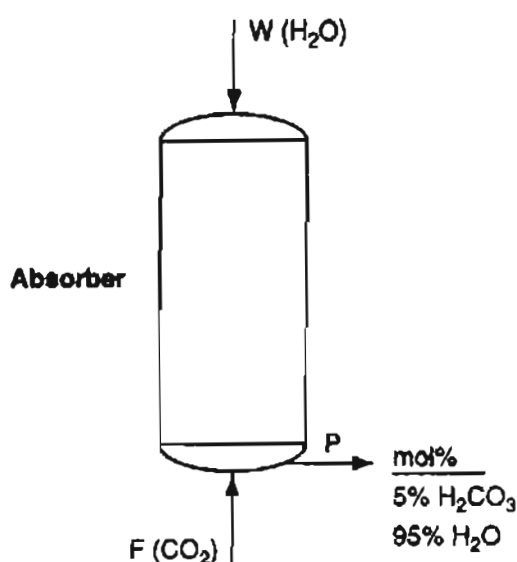


Figure 10.2 Schematic of the CO_2 absorber.

to solve for W , F , and P , but you can't! Try it. The reason is that the three element balances are not independent. Only two of the element balances are independent. If you pick a basis of $P = 100$ mol, the degrees of freedom become zero, and then you can solve for W and F . If you are curious as to why the three element balances are not independent, you can view H_2CO_3 as $H_2O \cdot CO_2$ in which the fixed ratio of H/O and C/O prevents the O balance from being independent of the H and C balances. Refer to Appendix L1 for information as to how to determine whether a set of material balance equations is independent.

EXAMPLE 10.5 Solution of Examples 10.1 and 10.3 Using Element Balances

All of the given data for this example is the same as in Examples 10.1 and 10.3

Solution

Example 10.1

Instead of the degree-of-freedom analysis in Steps 6 and 7 of Example 10.1, the following applies when element balances are used:

Number of variables: 10 (ξ is not involved)

Number of equations: 10

Basis: $F = 100$

Element material balances: 4 (independent)

C, H, Cl, N

Specifications: 3 as in Example 10.1

Implicit equations: 2 as in Example 10.1

The degrees of freedom are zero.

In Steps 8 and 9 the element material balances are:

$$\text{C: } 100(0.40) = n_{\text{CH}_4}^{\text{out}}(1) + n_{\text{CH}_3\text{Cl}}^{\text{out}}(1)$$

$$\text{H: } 100(0.40)(4) = n_{\text{CH}_4}^{\text{out}}(4) + n_{\text{HCl}}^{\text{out}}(1) + n_{\text{CH}_3\text{Cl}}^{\text{out}}(3)$$

$$\text{Cl: } 100(0.50)(2) = n_{\text{Cl}_2}^{\text{out}}(2) + n_{\text{HCl}}^{\text{out}}(1) + n_{\text{CH}_3\text{Cl}}^{\text{out}}(1)$$

$$2\text{N: } 100(0.10)(1) = n_{\text{N}_2}^{\text{out}}(1)$$

Substitute these equations for the species balances used in Example 10.1. As expected, the solution of the problem will be the same as found in Example 10.1.

Example 10.3

The degree-of-freedom analysis in Steps 6 and 7 is:

Variables: 9 (ξ_1 and ξ_2 are not involved)

Equations: 9

Basis: $F = 1$

Element balances: 4 (independent)

C, H, O, N

Specifications: 3 (the same as in Example 10.3)

Implicit equations: 1 (the same as in Example 10.3)

The degrees of freedom are zero.

In Steps 8 and 9 the element balances are:

$$\text{C: } 1(1) + 4.76(0) = P[y_{\text{CH}_3\text{OH}}^P(1) + y_{\text{CH}_2\text{O}}^P(1) + y_{\text{CO}}^P(1)]$$

$$\text{H: } 1(4) + 4.76(0) = P[y_{\text{CH}_3\text{OH}}^P(4) + y_{\text{CH}_2\text{O}}^P(2) + y_{\text{H}_2\text{O}}^P(2)]$$

$$\text{O: } 1(1) + 1.00(2) = P[y_{\text{CH}_3\text{OH}}^P(1) + y_{\text{O}_2}^P(2) + y_{\text{CH}_2\text{O}}^P(1) + y_{\text{H}_2\text{O}}^P(1) + y_{\text{CO}}^P(1)]$$

$$2\text{N: } 1(0) + 3.76 = P[y_{\text{N}_2}^P(1)]$$

Substitute these equations for the species balances used in Example 10.3. The solution of the problem will not change.

It would be easier to use the term $y_i^P P = n_i^P$ in the equations above in place of the product of two variables, y_i^P and P .

Element balances are especially useful when you do not know what reactions occur in a process. You only know information about the input and output stream components, as illustrated by the next example.

EXAMPLE 10.6 Use of Element Balances to Solve a Hydrocracking Problem

Hydrocracking is an important refinery process for converting low-valued heavy hydrocarbons into more valuable lower molecular weight hydrocarbons by exposing the feed to a zeolite catalyst at high temperature and pressure in the presence of hydrogen. Researchers in this field study the hydrocracking of pure components, such as octane (C_8H_{18}), to understand the behavior of cracking reactions. In one such experiment for the hydrocracking of octane, the cracked products had the following composition in mole percent: 19.5% C_3H_8 , 59.4% C_4H_{10} , and 21.1% C_5H_{12} . You are asked to determine the molar ratio of hydrogen consumed to octane reacted for this process.

Solution

We will use element balances to solve this problem because the reactions involved in the process are not specified.

Steps 1, 2, 3, and 4

Figure E10.6 is a sketch of the laboratory hydrocracker reactor together with the data for the streams.

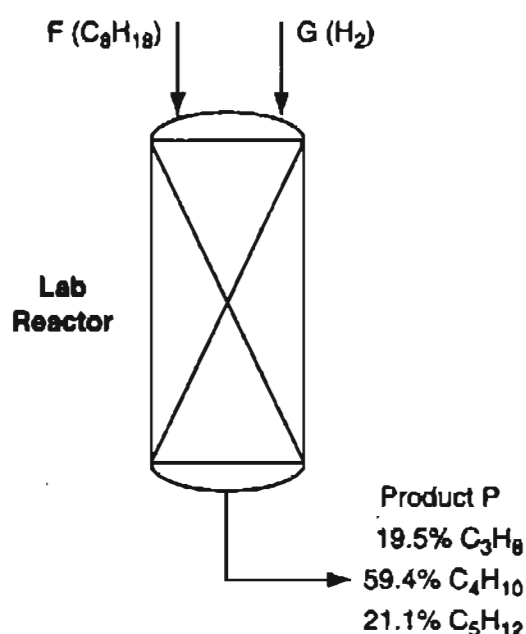


Figure E10.6

Step 5 Basis: $P = 100$ g mol

Steps 6 and 7

The degree-of-freedom analysis is

Variables: 3

F, G, P

Equations: 3

Element balances: 2

H, C

Basis: $P = 100$

If you calculate the degrees of freedom based on species balances, you have as unknowns five species molar flows, P , and R (the number of independent reaction equations which equals the number of unknown extents of reaction), and as equations five species balances, one specification (the basis), and one implicit equation so that

$$\text{degrees of freedom} = (6 + R) - (5 + 2) = R - 1$$

Thus, although you do not know what R is from the problem statement, for zero degrees of freedom to occur, $R = 1$, that is, one independent reaction equation exists. You can be assuaged that if you do not know R and a minimum reaction set, and thus you do not know how to involve the respective ξ in the species equations, you can fall back on element balances.

Step 8

The element balances after introducing the specification and basis are:

$$\text{C: } F(8) + G(0) = 100[(0.195)(3) + (0.594)(4) + (0.211)(5)]$$

$$\text{H: } F(18) + G(2) = 100[(0.195)(8) + (0.594)(10) + (0.211)(12)]$$

and the solution is

$$F = 50.2 \text{ g mol} \qquad G = 49.8 \text{ g mol}$$

The ratio

$$\frac{\text{H}_2 \text{ consumed}}{\text{C}_8\text{H}_{18} \text{ reacted}} = \frac{49.8 \text{ g mol}}{50.2 \text{ g mol}} = 0.992$$

You will find that employing element material balances can be simpler than employing the extent of reaction for problems in which the reaction equations are not specifically known or must be inferred, as shown in the examples in the next section.

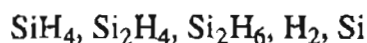
SELF-ASSESSMENT TEST

Questions

1. Do you have to write element material balances with the units of each term being moles rather than mass? Explain your answer.
2. Will the degrees of freedom be smaller or larger using element balances in place of species balances?
3. How can you determine whether a set of element balances is independent?
4. Can the number of independent element balances ever be larger than the number of species balances in a problem?

Problems

1. Consider a system used in the manufacture of electronic materials (all gases except Si)



How many independent element balances can you make for this system?

2. Methane burns with O_2 to produce a gaseous product that contains CH_4 , O_2 , CO_2 , CO , H_2O , and H_2 . How many independent element balances can you write for this system?
3. Solve the Self-Assessment Test problems in Section 10.1 using element balances.

Discussion Problem

1. Read Discussion Question #2 in Section 10.1. How would you use element balances in analyzing the process?

10.3 Material Balances Involving Combustion

In this section we discuss combustion as an extension of the previous discussion about chemical reactions. Combustion is the reaction of a substance with oxygen with the associated release of energy and generation of product gases such as H_2O , CO_2 , CO , and SO_2 . Typical examples of combustion are the combustion of coal, heating oil, and natural gas used to generate electricity in utility power stations, and engines that operate using the combustion of gasoline or diesel fuel. Most combustion processes use air as the source of oxygen. For our purposes you can assume that air contains 79% N_2 and 21% O_2 (see Chapter 2 for a more detailed analysis), neglecting the other components with a total of less than 1.0%, and can assume that air has an average molecular weight of 29. Although a small amount of N_2 oxidizes to NO and NO_2 , gases called NO_x , a pollutant, the amount is so small that we treat

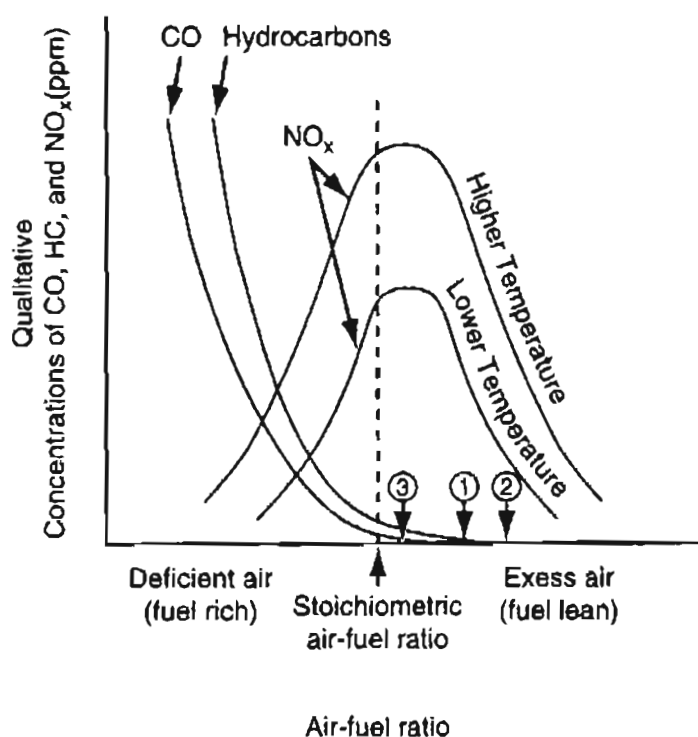


Figure 10.3 Pollutants resulting from combustion vary with the air-to-fuel ratio and the temperature of combustion. The fuel is natural gas. Hydrocarbons and CO increase with deficient air. Efficiency decreases with too much excess air, but so does the NO_x . (1) Normal operating state. (2) Operating state driven by NO_x limits. (3) Minimum excess O_2 to be below CO limits.

N_2 as a nonreacting component of air and fuel. Figure 10.3 shows how the CO, unburned hydrocarbons, and NO_x vary with the air-to-fuel ratio in combustion.

Combustion requires special attention because of some of the terminology involved. You should become acquainted with these special terms:

- a. **Flue or stack gas**—all the gases resulting from a combustion process including the water vapor, sometimes known as a **wet basis**.
- b. **Orsat analysis or dry basis**—all the gases resulting from a combustion process *not including the water vapor*. (Orsat analysis refers to a type of gas analysis apparatus in which the volumes of the respective gases are measured over and in equilibrium with water; hence each component is saturated with water vapor. The net result of the analysis is to eliminate water as a component that is measured.) Look at Figure 10.4. To convert from one analysis to another, you have to adjust the percentages of the components to the desired basis as explained in Chapter 2.
- c. **Complete combustion**—the complete reaction of the hydrocarbon fuel producing CO_2 , SO_2 , and H_2O .
- d. **Partial combustion**—the combustion of the fuel producing at least some CO. Because CO itself can react with oxygen, the production of CO in a combustion process does not produce as much energy as it would if only CO_2 were produced.
- e. **Theoretical air (or theoretical oxygen)**—the minimum amount of air (or oxygen) required to be brought into the process **for complete combustion**. Sometimes this quantity is called the **required air** (or oxygen).

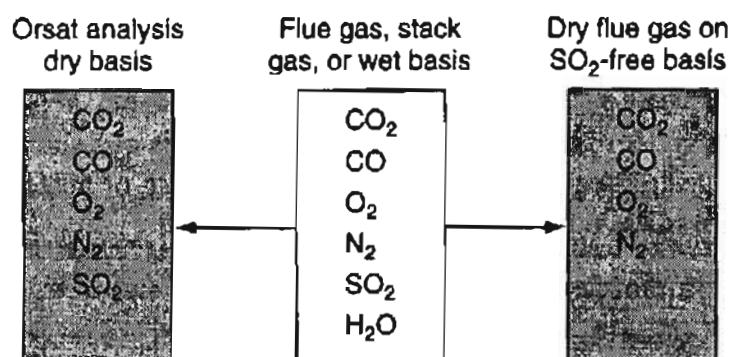


Figure 10.4 Comparison of a gas analysis on different bases.

- f. **Excess air (or excess oxygen)**—in line with the definition of excess reactant given in Chapter 9, excess air (or oxygen) is the amount of air (or oxygen) in excess of that required for complete combustion as defined in (e).

The calculated amount of *excess air does not depend on how much material is actually burned but what is possible to be burned*. Even if only partial combustion takes place, as, for example, C burning to both CO and CO₂, the excess air (or oxygen) is computed as if the process of combustion went to completion and produced only CO₂. Do not ever forget this basic assumption!

The percent excess air is identical to the percent excess O₂ (often a more convenient calculation):

$$\% \text{ excess air} = 100 \frac{\text{excess air}}{\text{required air}} = 100 \frac{\text{excess O}_2/0.21}{\text{required O}_2/0.21} \quad (10.8)$$

Note that the ratio 1/0.21 of air to O₂ cancels out in Equation (10.8). Percent excess air may also be computed as

$$\% \text{ excess air} = 100 \frac{\text{O}_2 \text{ entering process} - \text{O}_2 \text{ required}}{\text{O}_2 \text{ required}} \quad (10.9)$$

or

$$\% \text{ excess air} = 100 \frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2} \quad (10.10)$$

The precision achieved from these different relations to calculate the percent excess air may not be the same because when you take differences in large numbers that involve some error, the relative error in the difference is even bigger.

In calculating the degrees of freedom in a problem, if the percent of excess air and the chemical equation are specified in the problem, you can calculate how much air enters with the fuel, hence the number of equations involved is increased by one, or the number of unknowns is reduced by one.

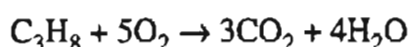
Now, let us explore these concepts via some examples.

EXAMPLE 10.7 Excess Air

Fuels other than gasoline are being eyed for motor vehicles because they generate lower levels of pollutants than does gasoline. Compressed propane is one such proposed fuel. Suppose that in a test 20 kg of C_3H_8 is burned with 400 kg of air to produce 44 kg of CO_2 and 12 kg of CO . What was the percent excess air?

Solution

This is a problem involving the following reaction (is the reaction equation correctly balanced?)



Basis: 20 kg of C_3H_8

Since the percentage of excess air is based on the *complete combustion* of C_3H_8 to CO_2 and H_2O , the fact that combustion is not complete has no influence on the calculation of "excess air." The required O_2 is

$$\frac{20 \text{ kg } C_3H_8}{1} \left| \frac{1 \text{ kg mol } C_3H_8}{44.09 \text{ kg } C_3H_8} \right| \left| \frac{5 \text{ kg mol } O_2}{1 \text{ kg mol } C_3H_8} \right| = 2.27 \text{ kg mol } O_2$$

The entering O_2 is

$$\frac{400 \text{ kg air}}{1} \left| \frac{1 \text{ kg mol air}}{29 \text{ kg air}} \right| \left| \frac{21 \text{ kg mol } O_2}{100 \text{ kg mol air}} \right| = 2.90 \text{ kg mol } O_2$$

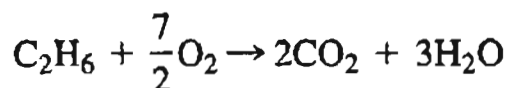
The percentage of excess air is

$$100 \times \frac{\text{excess } O_2}{\text{required } O_2} = 100 \times \frac{\text{entering } O_2 - \text{required } O_2}{\text{required } O_2}$$

$$\% \text{ excess air} = \frac{2.90 \text{ lb mol } O_2 - 2.27 \text{ lb mol } O_2}{2.27 \text{ lb mol } O_2} \left| \frac{100}{1} \right| = 28\%$$

In calculating the amount of excess air, remember that the excess is the amount of air that enters the combustion process over and above that required for complete combustion. Suppose there is some oxygen in the material being burned. For example, suppose that a gas containing 80% C_2H_6 and 20% O_2 is burned in an engine with 200% excess air. Eighty percent of the ethane goes to CO_2 , 10% goes to CO , and 10% remained unburned. What is the amount of the excess air per 100 moles of the gas? First, you can ignore the information about the CO and the unburned ethane because the basis of the calculation of excess air is *complete combustion*. Specifically C goes to CO_2 , S to SO_2 , H₂ to H_2O , CO goes to CO_2 , and so on.

Second, the oxygen in the fuel cannot be ignored. Based on the reaction



80 moles of C_2H_6 require $3.5(80) = 280$ moles of O_2 for complete combustion. However, the gas contains 20 moles of O_2 , so that only $280 - 20 = 260$ moles of O_2 are needed in the entering air for complete combustion. Thus, 260 moles of O_2 are the required O_2 , and the calculation of the 200% excess O_2 (air) is based on 260, not 280, moles of O_2 :

<u>Entering with air</u>	<u>Moles O_2</u>
required O_2 :	260
excess O_2 (2)(260):	<u>520</u>
total O_2 (3)(260):	780

In the following problems each step cited in Chapter 7 will be identified so that you can follow the strategy of the solution.

Example 10.8 A Fuel Cell to Generate Electricity From Methane

"A Fuel Cell in Every Car" is the headline of an article in *Chemical and Engineering News*, March 5, 2001, p. 19. In essence, a fuel cell is an open system into which fuel and air are fed, and out of which comes electricity and waste products. Figure E10.8 is a sketch of a fuel cell in which a continuous flow of methane (CH_4)

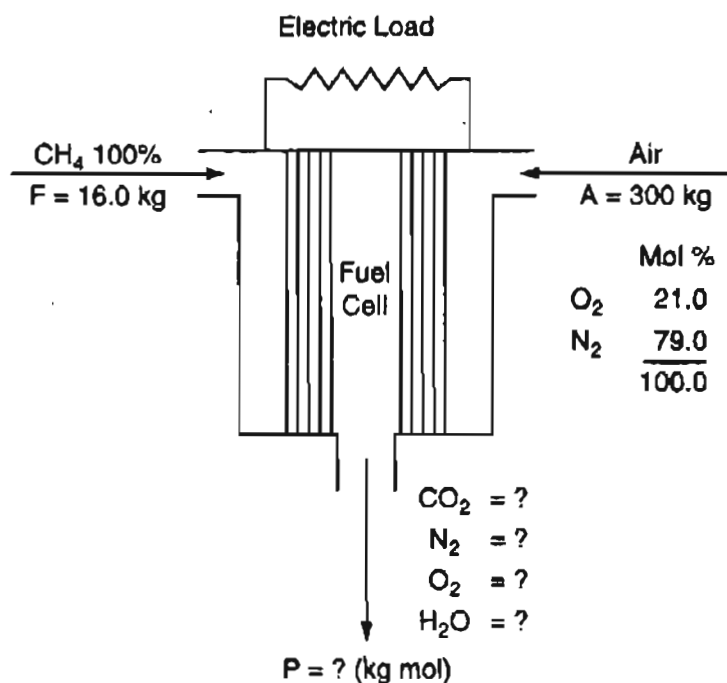


Figure E10.8

and air (O_2 plus N_2) produce electricity plus CO_2 and H_2O . Special membranes and catalysts are needed to promote the reaction of CH_4 .

Based on the data given in Figure E10.8, you are asked to calculate the composition of the products in P .

Solution

Steps 1, 2, 3, and 4 This is a steady-state process with reaction. Can you assume a complete reaction occurs? Yes. No CH_4 appears in P . The system is the fuel cell (open, steady state). Because the process output is a gas, the composition will be mole fractions or moles, hence it is more convenient to use moles rather than mass in this problem even though the quantities of CH_4 and air are stated in kg. You can carry out the necessary preliminary conversions as follows:

$$\frac{300 \text{ kg A}}{29.0 \text{ kg A}} \left| \frac{1 \text{ kg mol A}}{29.0 \text{ kg A}} \right| = 10.35 \text{ kg mol A in}$$

$$\frac{16.0 \text{ kg } CH_4}{16.0 \text{ kg } CH_4} \left| \frac{1 \text{ kg mol } CH_4}{16.0 \text{ kg } CH_4} \right| = 1.00 \text{ kg mol } CH_4 \text{ in}$$

$$\frac{10.35 \text{ kg mol A}}{1 \text{ kg mol A}} \left| \frac{0.21 \text{ kg mol } O_2}{1 \text{ kg mol A}} \right| = 2.17 \text{ kg mol } O_2 \text{ in}$$

$$\frac{10.35 \text{ kg mol A}}{1 \text{ kg mol A}} \left| \frac{0.79 \text{ kg mol } N_2}{1 \text{ kg mol A}} \right| = 8.18 \text{ kg mol } N_2 \text{ in}$$

Step 5 Since no particular basis is designated we will pick a convenient basis

Basis: 16.0 kg CH_4 entering = 1 kg mol CH_4

Steps 6 and 7

The degree-of-freedom analysis is (A has been calculated):

Variables: 8

$$F, P, n_{CO_2}^P, n_{N_2}^P, n_{O_2}^P, n_{H_2O}^P, n_{O_2}^A, n_{N_2}^A,$$

Equations: 8

Basis: $F = 1 \text{ kg mol}$

Element material balances: 4 (independent)

C, H, O, N

Specifications and calculated quantities: 2

$$n_{O_2}^A = 2.17, n_{N_2}^A = 8.18$$

Implicit equation: 1

$$\sum n_i^P = P$$

The degrees of freedom are zero.

If you use species balances in solving the problem, you have to involve the reaction: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$: Then (A has been calculated)

Variables: 10

$F, P, n_{\text{O}_2}^A, n_{\text{N}_2}^A, n_{\text{CH}_4}^P, n_{\text{CO}_2}^P, n_{\text{N}_2}^P, n_{\text{O}_2}^P, n_{\text{H}_2\text{O}}^P, \xi$

Equations: 10

Basis: $F = 1$

Species balances: 5

Calculated quantities: 2 (as above)

Specifications: 1

$\xi = 1$ (because the reaction is complete)

Implicit equation: 1

$$\sum n_i^P = P$$

Step 8

After introduction of the specified and calculated quantities, the element material balances are (in moles):

	Out		In
C:	$n_{\text{CO}_2}^P(1)$	=	1(1)
H:	$n_{\text{H}_2\text{O}}^P(2)$	=	1(4)
O:	$n_{\text{CO}_2}^P(2) + n_{\text{O}_2}^P(2) + n_{\text{H}_2\text{O}}^P(1)$	=	2.17(2)
2N:	$n_{\text{N}_2}^P$	=	8.18

The species material balances are:

Compound	Out	In	$\nu_i \xi$	g mol
CH_4 :	$n_{\text{CH}_4}^P = 1.0$	-	$1 \times 1 = 0$	
O_2 :	$n_{\text{O}_2}^P = 2.17$	-	$2 \times 1 = 0.17$	
N_2 :	$n_{\text{N}_2}^P = 8.18$	-	$0 \times 1 = 8.18$	
CO_2 :	$n_{\text{CO}_2}^P = 0$	+	$1 \times 1 = 1.0$	
H_2O :	$n_{\text{H}_2\text{O}}^P = 0$	+	$2 \times 1 = 2.0$	

Step 9

The solution of either set of equations gives

$$n_{\text{CH}_4}^P = 0, n_{\text{O}_2}^P = 0.17, n_{\text{N}_2}^P = 8.18, n_{\text{CO}_2}^P = 1.0, n_{\text{H}_2\text{O}}^P = 2.0, P = 11.35$$

and the mole percentage composition of P is

$$y_{\phi_2} = 1.5\%, y_{N_2} = 72.1\%, y_{CO_2} = 8.8\%, \text{ and } y_{H_2O} = 17.6\%$$

Step 10

You can check the answer by determining the total mass of the exit gas and comparing it to total mass entering (316 kg), but we will omit this step here to save space.

Example 10.9 Combustion of Coal

A local utility burns coal having the following composition on a dry basis. (Note that the coal analysis below is a convenient one for our calculations, but is not necessarily the only type of analysis that is reported for coal. Some analyses contain much less information about each element.)

Component	Percent
C	83.05
H	4.45
O	3.36
N	1.08
S	0.70
Ash	7.36
Total	100.0

The average Orsat analysis of the gas from the stack during a 24-hour test was

Component	Percent
CO ₂ + SO ₂	15.4
CO	0.0
O ₂	4.0
N ₂	80.6
Total	100.0

Moisture in the fuel was 3.90%, and the air on the average contained 0.0048 lb H₂O/lb dry air. The refuse showed 14.0% unburned coal, with the remainder being ash.

You are asked to check the consistency of the data before they are stored in a database. Is the consistency satisfactory? What was the average percent excess air used?

Solution

This is an open, steady-state process with reaction. The system is the furnace.

All of the information given in the problem statement has been placed on Figure E10.9. Because the gas analysis is on a dry basis, we added a flowstream *W* for the exit water to the process diagram.

The compositions of *F* and *R* are given in mass, and those of *P* and *A* in moles.

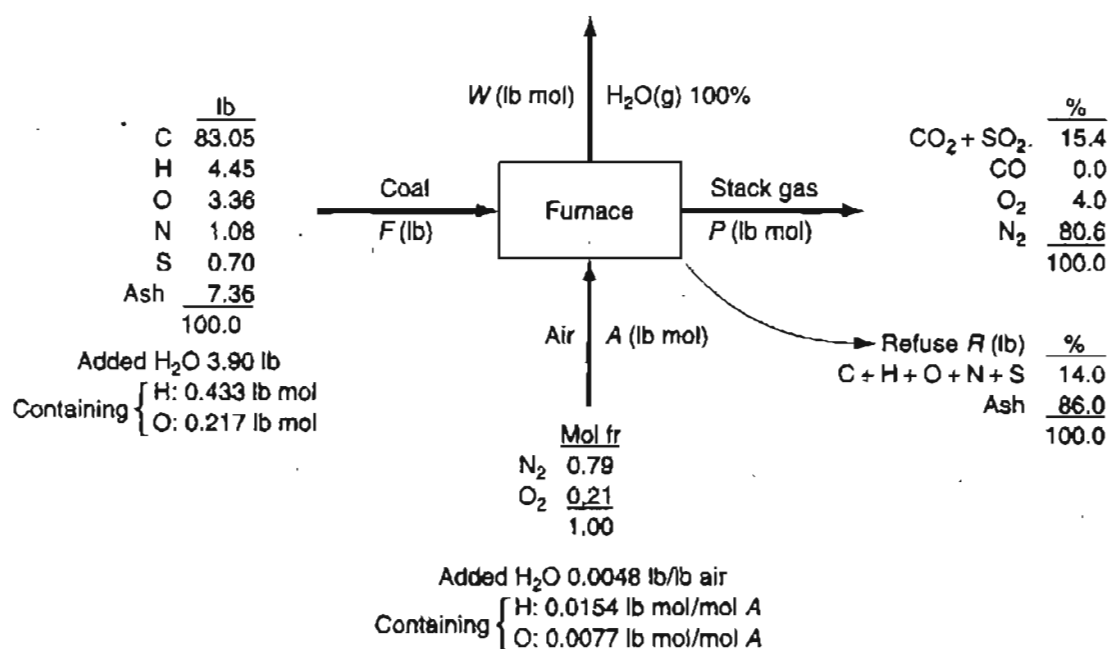


Figure E10.9

Step 5 Pick a basis of $F = 100$ lb as convenient.

Step 4 (repeated) You must first calculate some extra information besides the compositions given in the diagram (the information has already been added to Figure E10.9 for convenience).

H₂O in coal:

$$\frac{3.90 \text{ lb H}_2\text{O}}{18 \text{ lb H}_2\text{O}} \left| \frac{1 \text{ lb mol H}_2\text{O}}{1 \text{ lb mol H}_2\text{O}} \right| \frac{2 \text{ lb mol H}}{1 \text{ lb mol H}_2\text{O}} = 0.433 \text{ lb mol H}$$

(with 0.217 lb mol O)

H₂O in air:

$$\frac{0.0048 \text{ lb H}_2\text{O}}{1 \text{ lb air}} \left| \frac{29 \text{ lb air}}{1 \text{ lb mol air}} \right| \frac{1 \text{ lb mol H}_2\text{O}}{18 \text{ lb H}_2\text{O}} = 0.0077 \frac{\text{lb mol H}_2\text{O}}{\text{lb mol air}}$$

(with 0.0154 lb mol H/lb mol A)
 (with 0.0077 lb mol O/lb mol A)

You might neglect the C, H, O, N, and S in the refuse, but we will include the amount to show what calculations would be necessary if the amounts of the elements were significant. To do so, we must make a preliminary mass balance for the ash

$$\text{ash balance (lb): } 7.36 = 0.86(R)$$

$$R = 8.56 \text{ lb}$$

The unburned coal in the refuse is

$$8.56(0.14) = 1.20 \text{ lb}$$

If we assume that the combustibles in the refuse occur in the same proportions as they do in the coal (which may not be true), the quantities of the combustibles in R on an ash-free basis are:

Component	mass %	lb	lb mol
C	89.65	1.076	0.0897
H	4.80	0.058	0.0537
O	3.63	0.0436	0.0027
N	1.17	0.014	0.0010
S	<u>0.76</u>	<u>0.009</u>	<u>0.0003</u>
	100.00	1.20	0.1474

Steps 6 and 7

You can write only four element balances because S and C must be combined inasmuch as these two elements are combined in the stack gas analysis. Presumably one of the four equations is redundant and can be used to check the calculations. You can examine the composite matrix (see Appendix L) if you wish to find its rank.

The degree-of-freedom analysis is

Variables: 4

F, A, W, P

Equations: 5

Basis: $F = 100$

Element balances: 4

H, O, N, S + C

To use a degree-of-freedom analysis based on species would be quite complex, and will be omitted.

Step 8

The element balances in moles are

	<i>In</i>			<i>Out</i>		
	F	A	W	P	R	
C + S:	$\frac{83.05}{12.0} + \frac{0.70}{32.0}$	0	= 0	+ $P(0.154)$	+ 0.0897+0.0003	
H:	$\frac{4.45}{1.008} + 0.433$	+ 0.0154 A	= 2W	+ 0	+ 0.0537	
O:	$\frac{3.36}{16.0} + 0.217$	+ 0.21A(2)+0.007A	= W	+ 2P(0.154+0.040)	+ 0.0027	
N:	$\frac{1.08}{14.0} +$	2(0.79A)	= 0	+ 2P(0.806)	+ 2(0.001)	

Step 9

Solve the equations on a computer, or by hand in this order: C + S to get P, N to get A, and H to get W. The values are (in moles) $P = 44.5$, $A = 45.4$, and $W = 2.747$.

Step 10

Use the O balance to check the results

$$19.8 = 20.3$$

The difference is about 1%. Inasmuch as the data provided are actual measurements, in view of the random and possibly biased errors in the data, the round-off error introduced in the calculations, and possible leaks in the furnace, the data seem to be quite satisfactory. Try calculating W, a small number, from both the H and O balances. What size error do you find?

To calculate the excess air, because of the oxygen in the coal and the existence of unburned combustibles, we will calculate the total oxygen in and the required oxygen:

$$\% \text{ excess air} = 100 \times \frac{\text{O}_2 \text{ entering} - \text{O}_2 \text{ required}}{\text{O}_2 \text{ required}}$$

Assume that no oxygen is required by the ash. The required O_2 is

Component	Reaction	lb	lb mol	Required O_2 (lb mol)
C	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	83.05	6.921	6.921
H	$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$	4.45	<u>4.415</u> H	1.104
O	—	3.36	0.210	(0.105)
N	—	—	—	—
S	$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$	0.70	0.022	<u>0.022</u>
				7.942

and the oxygen entering in the air is $(45.35)(0.21) = 9.524$ lb mol.

$$\% \text{ excess air} = 100 \times \frac{9.524 - 7.942}{7.942} = 19.9\%$$

If you (incorrectly) calculated the % excess air from the wet stack gas analysis alone, you would get

$$100 \times \frac{4.0}{15.4 + 2.746/2} = 23.8\%$$

From the viewpoint of the increases of the CO_2 concentration in the atmosphere, would the CH_4 in Example 10.8 or the coal in Example 10.9 contribute more CO_2 per kg? The H/C ratio in moles in CH_4 was 4/1, whereas in the coal it was $0.0537/0.0897 = 0.60$. Figure 10.5 shows how the H/C ratio varies with different types of fuel.

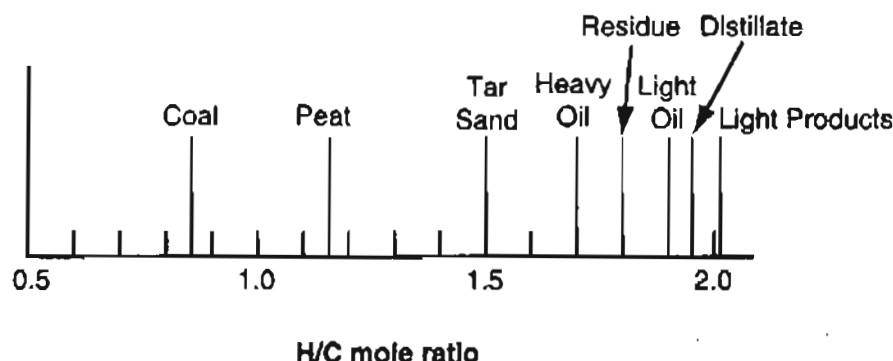


Figure 10.5 Variation of the H/C mole ratio in selected fuels.

SELF-ASSESSMENT TEST

Questions

1. Explain the difference between a flue gas analysis and an Orsat analysis; wet basis and dry basis.
2. What does an SO_2 -free basis mean?
3. Write down the equation relating percent excess air to the required air and entering air.
4. Will the percent excess air always be the same as the percent excess oxygen in combustion (by oxygen)?
5. In a combustion process in which a specified percentage of excess air is used, and in which CO is one of the products of combustion, will the analysis of the resulting exit gases contain more or less oxygen than if all the carbon had burned to CO_2 ?

6. Answer the following questions true or false.
- Excess air for combustion is calculated using the assumption of complete reaction whether or not a reaction takes place.
 - For the typical combustion process the products are CO_2 gas and H_2O vapor.
 - In combustion processes, since any oxygen in the coal or fuel oil is inert, it can be ignored in the combustion calculations.
 - The concentration of N_2 in a flue gas is usually obtained by direct measurement.

Problems

1. Pure carbon is burned in oxygen. The flue gas analysis is:

CO_2	75 mol %
CO	14 mol %
O_2	11 mol %

What was the percent excess oxygen used?

- Toluene, C_7H_8 , is burned with 30% excess air. A bad burner causes 15% of the carbon to form soot (pure C) deposited on the walls of the furnace. What is the Orsat analysis of the gases leaving the furnace?
- A synthesis gas analyzing CO_2 : 6.4%, O_2 : 0.2%, CO : 40.0%, and H_2 : 50.8% (the balance is N_2) is burned with excess dry air. The problem is to determine the composition of the flue gas. How many degrees of freedom exist in this problem, that is, how many additional variables must be specified?
- ✓ A coal analyzing 65.4% C, 5.3% H, 0.6% S, 1.1% N, 18.5% O, and 9.1% ash is burned so that all combustible is burnt out of the ash. The flue gas analyzes 13.00% CO_2 , 0.76% CO , 6.17% O_2 , 0.87% H_2 , and 79.20% N_2 . All of the sulfur burns to SO_2 , which is included in the CO_2 in the gas analysis (i.e., $\text{CO}_2 + \text{SO}_2 = 13.00\%$). Calculate:
 - Pounds of coal fired per 100 lb mol of dry flue gas as analyzed;
 - Ratio of moles of total combustion gases to moles of dry air supplied;
 - Total moles of water vapor in the stack gas per 100 lb of coal if the entering air is dry;
 - Percent excess air.
- A hydrocarbon fuel is burnt with excess air. The Orsat analysis of the flue gas shows 10.2% CO_2 , 1.0% CO , 8.4% O_2 , and 80.4% N_2 . What is the atomic ratio of H to C in the fuel?

Thought Problems

- In a small pharmaceutical plant, it had not been possible for a period of two months to get more than 80% of rated output from a boiler rated at 120,000 lb of steam per hour. The boiler had complete flow metering and combustion control equipment, but the steam flow could not be brought to more than 100,000 lb/hr.

What would you recommend be done to find the cause(s) of the problem and alleviate it?
- In connection with the concern about global warming, because of the increase in CO_2 concentration in the atmosphere, would you recommend the use of coal, ethanol, fuel oil, or natural gas as a fuel?

Discussion Problems

1. In-situ bioremediation of subsurface materials contaminated with organic compounds is being evaluated by the EPA and by industry as one technique for managing hazardous wastes. The process usually involves stimulating the indigenous subsurface microflora to degrade the contaminants in place, although microorganisms with specialized metabolic capabilities have been added in some cases. The ultimate goal of biodegradation is to convert organic wastes into biomass and harmless byproducts of microbial metabolism such as CO_2 , CH_4 , and inorganic salts.

Bioremediation of trichloroethylene, and *cis*- and *trans*-dichloroethylene was investigated in a test plot in a field trial. The aquifer was not pretreated with methane and oxygen to stimulate growth of the methanotrophs. The biotransformation of *trans*-dichloroethylene, *cis*-dichloroethylene, and trichloroethylene added at 50, 110, and 130 $\mu\text{g/L}$ was 65, 45, and 25%, respectively, which suggests that the less-chlorinated compounds are more readily degraded than are the highly chlorinated compounds.

What other influences might have affected the results obtained?

2. Suppose you are asked to serve as a consultant on the problem of how to produce oxygen on the moon as economically as possible. The raw material readily available is FeTiO_3 , SiO_2 , and/or FeO . The energy to carry out the reactions is presumably available from the sun or atomic energy that provides electricity or high pressure steam. Discuss some possible methods of O_2 generation and draw a simple flowsheet for the process.

Some very useful references pertaining to this problem are (a) L. A. Taylor, "Rocks and Minerals in the Regolith of the Moon: Resources for a Lunar Base," pp. 29–47 in *Advanced Materials—Applications Mining and Metallurgical Processing Principles*, ed. V. I. Lakshmanan, Soc. Mining, Mineral, & Exploration, Littleton, CO (1988); (b) L. A. Taylor, "Resources for a Lunar Base: Rocks, Minerals and Soils of the Moon," in *2nd Symp. on Lunar Base and Space Activities of the 21st Century*, ed. W. W. Mendell, Lunar & Planetary Inst., Houston, TX (1993); (c) L. A. Taylor and D. W. Carrier, "Oxygen Production Processes on the Moon: An Overview and Evaluation," *Resources in New-Earth Space*, Univ. Arizona Press, Tucson, AZ (1993).

Looking Back

In this chapter we applied Equation (10.1) and its analogs to processes involving reaction. If you make element balances, the generation and consumption terms in Equation (10.1) are zero. If you make species balances, the accumulation and consumption terms are not zero, and you have to use the extent of reaction. Both open and closed systems with reaction thus admit no new principles. You simply apply the general material balance with reaction to these systems recognizing their characteristics (e.g., closed systems have no flow into or out across the system boundary).

GLOSSARY OF NEW WORDS

Complete combustion The complete reaction of a reactant to produce CO_2 , SO_2 , and H_2O .

Element balances Material balances involving chemical elements.

Excess air (or oxygen) The amount of air (or oxygen) in excess of that required for complete combustion.

Flue or stack gas All of the gases resulting from combustion including the water vapor, also known as a wet basis.

Minimal set of reactions The smallest set of chemical reaction equations that includes all of the species involved in the reactions.

Orsat analysis Also known as a dry basis. All of the gases resulting from combustion *not including the water vapor*. (Orsat refers to a technique of gas analysis.)

Partial combustion Combustion that produces at least some CO .

Required air (or oxygen) The amount of air (or oxygen) required for complete reaction to occur (see Theoretical air).

Species balances Material balances involving chemical species.

Theoretical air (or oxygen) The amount of air (or oxygen) required to be brought into a process to accomplish complete combustion. Also known as required air (or oxygen).

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent:

Croce, A.E. "The Application of the Concept of Extent of Reaction," *J. Chem. Educ.*, **79**, 506–509 (2002).

de Nevers, N. *Physical and Chemical Equilibrium for Processes*. Wiley-Interscience, New York (2002).

Moulijn, J.A., M. Markkee, and A. Van Diepen. *Chemical Process Technology*. Wiley, New York (2001).

Web Sites

<http://voyager5.sdsu.edu/testcenter/features/states/states.html>

http://www.epin.ncsu.edu/apti/ol_2000/module1/materia/material/htm

www.johnzink.com

PROBLEMS

- *10.1 Pure A in gas phase enters a reactor. 50% of this A is converted to B through the reaction $A \rightarrow 3 B$. What is the mole fraction of A in the exit stream?

What is the extent of reaction?

- *10.2 One of the most common commercial methods for the production of pure silicon that is to be used for the manufacture of semiconductors is the Siemens process (see Figure P10.2) of chemical vapor deposition (CVD). A chamber contains a heated silicon rod, and a mixture of high purity trichlorosilane mixed with high purity hydrogen that is passed over the rod. Pure silicon (EGS-electronic grade silicon) deposits on the rod as a polycrystalline solid. (Single crystals of Si are later made by subsequently melting the EGS and drawing a single crystal from the melt.) The reaction is: $H_2(g) + SiHCl_3(g) \rightarrow Si(s) + 3HCl(g)$.

The rod initially has a mass of 1,460g, and the mole fraction of H_2 in the exit gas is 0.223. The mole fraction of H_2 in the feed to the reactor is 0.580, and the feed enters at the rate of 6.22 kg mol/hr. What will be the mass of the rod at the end of 20 minutes?

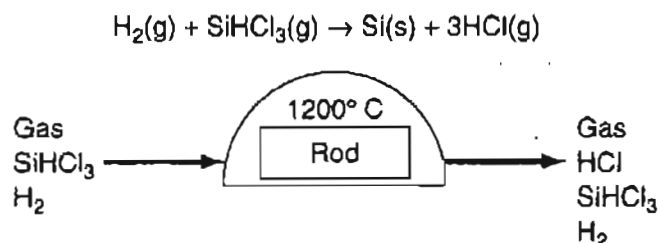


Figure P10.2

- *10.3 A low-grade pyrite containing 32% S is mixed with 10 lb of pure sulfur per 100 lb of pyrites so the mixture will burn readily with air, forming a burner gas that analyzes 13.4% SO_2 , 2.7% O_2 , and 83.9% N_2 . No sulfur is left in the cinder. Calculate the percentage of the sulfur fired that burned to SO_3 . (The SO_3 is not detected by the analysis.)
- *10.4 Examine the reactor in Figure P10.4. Your boss says something has gone wrong with the yield of CH_2O , and it is up to you to find out what the problem is. You start by making material balances (naturally!). Show all calculations. Is there some problem?

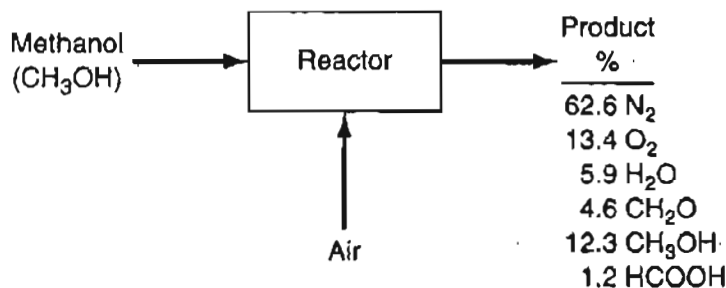


Figure P10.4

***10.5** A problem statement was:

A dry sample of limestone is completely soluble in HCl, and contains no Fe or Al. When a 1.000 g sample is ignited the loss in weight is found to be 0.450 g. Calculate the percent CaCO_3 and MgCO_3 in the limestone.

The solution was:

$$\frac{x}{84.3} + \frac{(1.000 - x)}{100} = \frac{0.450}{44}$$

$$100x + 84.3 - 84.3x = (0.450)(84.3)(100)/44$$

$$x = 0.121 \quad \text{MgCO}_3 = 12.1\%$$

$$\text{CaCO}_3 = 87.9\%$$

Answer the following questions:

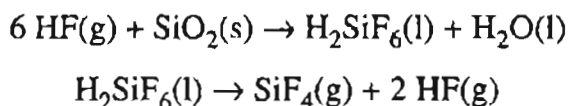
1. What information in addition to that in the problem statement had to be obtained?
2. What would a diagram for the process look like?
3. What was the basis for the problem solution?
4. What were the known variables in the problem statement, their values, and their units?
5. What were the unknown variables in the problem statement and their units?
6. What are the types of material balances that could be made for this problem?
7. What type(s) of material balance was made for this problem?
8. What was the degree of freedom for this problem?
9. Was the solution correct?

***10.6 In order to neutralize the acid in a waste stream (composed of H_2SO_4 and H_2O), dry ground limestone (composition 95% CaCO_3 and 5% inerts) is mixed in. The dried sludge collected from the process is only partly analyzed by firing it in a furnace which results in only CO_2 being driven off. By weight the CO_2 represents 10% of the dry sludge. What percent of the pure CaCO_3 in the limestone did not react in the neutralization?

**10.7 Copper as CuO can be obtained from an ore called Covellite which is comprised of CuS and gangue (inert solids). Only part of the CuS is oxidized with air to CuO. The gases leaving the roasting process analyze: SO_2 (7.2%), O_2 (8.1%), and N_2 (84.7%). Unfortunately, the method of gas analysis could not detect SO_3 in the exit gas, but SO_3 is known to exist.

Calculate the percent of the sulfur in the part of the CuS that reacts that forms SO_3 . Hint: you can consider the unreacted CuS as a compound that comes in and out of the process untouched, and thus is isolated from the process and can be ignored.

*10.8 A reactor is used to remove SiO_2 from a wafer in semiconductor manufacturing by contacting the SiO_2 surface with HF. The reactions are:



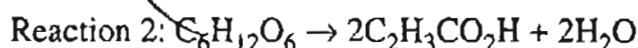
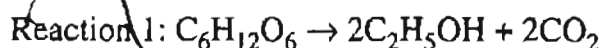
Assume the reactor is loaded with wafers having a silicon oxide surface, a flow of 50% HF and 50% nitrogen is started, and the reactions proceed.

In the reaction 10% of the HF is consumed. What is the composition of the exhaust stream?

✓ *10.9

3.61

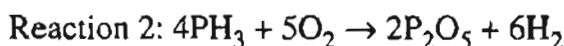
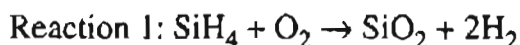
In the anaerobic fermentation of grain, the yeast *Saccharomyces cerevisiae* digests glucose from plants to form the products ethanol and propenoic acid by the following overall reactions:



In an open, flow reactor 3500 kg of a 12% glucose/water solution flow in. During fermentation, 120 kg of carbon dioxide are produced together with 90 kg of unreacted glucose. What are the weight percents of ethyl alcohol and propenoic acid that exit in the broth? Assume that none of the glucose is assimilated into the bacteria.

✓ **10.10

Semiconductor microchip processing often involves chemical vapor deposition (CVD) of thin layers. The material being deposited needs to have certain desirable properties. For instance, to overlay on aluminum or other bases, a phosphorus pentoxide-doped silicon dioxide coating is deposited as a passivation (protective) coating by the simultaneous reactions



Determine the relative masses of SiH_4 and PH_3 required to deposit a film of 5% by weight of phosphorus oxide (P_2O_5) in the protective coating.

**10.11

Printed circuit boards (PCBs) are used in the electronic industry to both connect and hold components in place. In production, 0.03 in. of copper foil is laminated to an insulating plastic board. A circuit pattern made of a chemically resistant polymer is then printed on the board. Next, the unwanted copper is chemically etched away by using selected reagents. If copper is treated with $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ (cupric ammonium chloride) and NH_4OH (ammonium hydroxide), the products are water and $\text{Cu}(\text{NH}_3)_4\text{Cl}$ (cuprous ammonium chloride). Once the copper is dissolved, the polymer is removed by solvents leaving the printed circuit ready for further processing. If a single-sided board 4 in. by 8 in. is to have 75% of the copper layer removed using the reagents above, how many grams of each reagent will be consumed? Data: The density of copper is 8.96 g/cm^3 .

**10.12

The thermal destruction of hazardous wastes involves the controlled exposure of waste to high temperatures (usually 900°C or greater) in an oxidizing environment. Types of thermal destruction equipment include high-temperature boilers, cement kilns, and industrial furnaces in which hazardous waste is burned as fuel. In a properly designed system, primary fuel (100% combustible material) is mixed with waste to produce a feed for the boiler.

(a) Sand containing 30% by weight of 4,4'-dichlorobiphenyl [an example of a polychlorinated biphenyl (PCB)] is to be cleaned by combustion with excess hexane

to produce a feed that is 60% combustible by weight. To decontaminate 8 tons of such contaminated sand, how many pounds of hexane would be required?

- (b) Write the two reactions that would take place under ideal conditions if the mixture of hexane and the contaminated sand were fed to the thermal oxidation process to produce the most environmentally satisfactory products. How would you suggest treating the exhaust from the burner? Explain.
- (c) The incinerator is supplied with an oxygen-enriched airstream containing 40% O_2 and 60% N_2 to promote high-temperature operation. The exit gas is found to have a $x_{CO_2} = 0.1654$ and $x_{O_2} = 0.1220$. Use this information and the data about the feed composition above to find: (1) the complete exit gas concentrations and (2) the % excess O_2 used in the reaction.

*10.13 A synthesis gas analyzing 6.4% CO_2 , 0.2% O_2 , 40.0% CO , and 50.8% H_2 , (the balance is N_2), is burned with 40% dry excess air. What is the composition of the flue gas?

✓ 3.44 *10.14 Hydrogen-free carbon in the form of coke is burned:

- (a) With complete combustion using theoretical air
 (b) With complete combustion using 50% excess air
 (c) Using 50% excess air but with 10% of the carbon burning to CO only.

In each case calculate the gas analysis that will be found by testing the flue gases on a dry basis.

*10.15 Thirty pounds of coal (analysis 80% C and 20% H ignoring the ash) are burned with 600 lb of air, yielding a gas having an Orsat analysis in which the ratio of CO_2 to CO is 3 to 2. What is the percent excess air?

✓ *10.16 A gas containing only CH_4 and N_2 is burned with air yielding a flue gas that has an Orsat analysis of CO_2 : 8.7%, CO : 1.0%, O_2 : 3.8%, and N_2 : 86.5%. Calculate the percent excess air used in combustion and the composition of the CH_4 - N_2 mixture.

*10.17 A natural gas consisting entirely of methane (CH_4) is burned with an oxygen enriched air of composition 40% O_2 and 60% N_2 . The Orsat analysis of the product gas as reported by the laboratory is CO_2 : 20.2%, O_2 : 4.1%, and N_2 : 75.7%. Can the reported analysis be correct? Show all calculations.

✓ 3.48 *10.18 Dry coke composed of 4% inert solids (ash), 90% carbon, and 6% hydrogen is burned in a furnace with dry air. The solid refuse left after combustion contains 10% carbon and 90% inert ash (and no hydrogen). The inert ash content does not enter into the reaction.

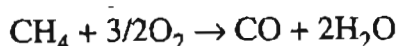
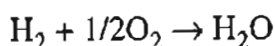
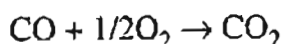
The Orsat analysis of the flue-gas gives 13.9% CO_2 , 0.8% CO , 4.3% O_2 , and 81.0% N_2 . Calculate the percent of excess air based on complete combustion of the coke.

*10.19 A gas with the following composition is burned with 50% excess air in a furnace. What is the composition of the flue gas by percent?

CH_4 :60%; C_2H_6 :20%; CO :5%; O_2 :5%; N_2 :10%

✓ 3.50 *10.20 A flare is used to convert unburned gases to innocuous products such as CO_2 and H_2O . If a gas of the following composition (in percent) is burned in the flare— CH_4 : 70%, C_3H_8 : 5%, CO : 15%, O_2 : 5%, N_2 : 5%—and the flue gas contains 7.73% CO_2 , 12.35% H_2O , and the balance is O_2 and N_2 , what was the percent excess air used?

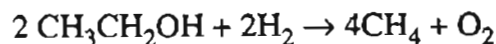
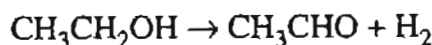
- *10.21 In underground coal combustion in the gas phase several reactions take place including



where the CO, H₂, and CH₄ come from coal pyrolysis.

If a gas phase composed of CO: 13.54%, CO₂: 15.22%, H₂: 15.01%, CH₄: 3.20%, and the balance N₂ is burned with 40% excess air, (a) how much air is needed per 100 moles of gas, and (b) what will be the analysis of the product gas on a wet basis?

- *10.22 Ethanol (CH₃CH₂OH) is dehydrogenated in the presence of air over a catalyst, and the following reactions take place



Separation of the product, CH₃CHO (acetaldehyde), as a liquid leaves an output gas with the following Orsat analysis:

CO₂:0.7%, O₂:2.1%, CO:2.3%, H₂:7.1%, CH₄:2.6%, and N₂:85.2%

How many kg of acetaldehyde are produced per kg of ethanol fed into the process?

- *10.23 Solvents emitted from industrial operations can become significant pollutants if not disposed of properly. A chromatographic study of the waste exhaust gas from a synthetic fiber plant has the following analysis in mole percent:

CS₂ 40%

SO₂ 10

H₂O 50

It has been suggested that the gas be disposed of by burning with an excess of air. The gaseous combustion products are then emitted to the air through a smokestack. The local air pollution regulations say that no stack gas is to analyze more than 2 percent SO₂ by an Orsat analysis averaged over a 24-hr period. Calculate the minimum percent excess air that must be used to stay within this regulation.

- *10.24 The products and byproducts from coal combustion can create environmental problems if the combustion process is not carried out properly. Your boss asks you to carry out an analysis of the combustion in boiler No. 6. You carry out the work assignment using existing instrumentation, and obtain the following data:

Fuel analysis (coal): 74% C, 14% H, and 12% ash

Flue gas analysis on a dry basis: 12.4% CO₂, 1.2% CO, 5.7% O₂ and 80.7% N₂

What are you going to report to your boss?

- *10.25 The Clean Air Act requires automobile manufacturers to warrant their control systems as satisfying the emission standards for 50,000 mi. It requires owners to have

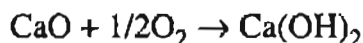
their engine control systems serviced exactly according to manufacturers' specifications and to always use the correct gasoline. In testing an engine exhaust having a known Orsat analysis of 16.2% CO₂, 4.8% O₂, and 79% N₂ at the outlet, you find to your surprise that at the end of the muffler the Orsat analysis is 13.1% CO₂. Can this discrepancy be caused by an air leak into the muffler? (Assume that the analyses are satisfactory.) If so, compute the moles of air leaking in per mole of exhaust gas leaving the engine.

- ✓**10.26 3.52 One of the products of sewage treatment is sludge. After microorganisms grow in the activated sludge process to remove nutrients and organic material, a substantial amount of wet sludge is produced. This sludge must be dewatered, one of the most expensive parts of most treatment plant operations.

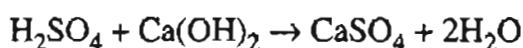
How to dispose of the dewatered sludge is a major problem. Some organizations sell dried sludge for fertilizer, some spread the sludge on farmland, and in some places it is burned. To burn a dried sludge, fuel oil is mixed with it, and the mixture is burned in a furnace with air. If you collect the following analysis for the sludge and for the product gas

Sludge (%)		Product Gas (%)	
S	32	SO ₂	1.52
C	40	CO ₂	10.14
H ₂	4	O ₂	4.65
O ₂	24	N ₂	81.67
		CO	2.02

- (a) Determine the weight percent of carbon and hydrogen in the fuel oil.
 (b) Determine the ratio of pounds of dry sludge to pounds of fuel oil in the mixture fed to the furnace.
- *10.27 Many industrial processes use acids to promote chemical reactions or produce acids from the chemical reactions occurring in the process. As a result, these acids many time end up in the wastewater stream from the process and must be neutralized as part of the wastewater treatment process before the water can be discharged from the process. Lime (CaO) is a cost effective neutralization agent for acid wastewater. Lime is dissolved in water by the following reaction:

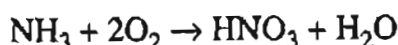


which reacts directly with acid, e.g., for H₂SO₄,



Consider an acidic wastewater stream with a flow rate of 1000 gal/min with an acid concentration of 2% H₂SO₄. Determine the flow rate of lime in lb/min necessary to neutralize the acid in this stream if 20% excess lime is used. Calculate the production rate of CaSO₄ from this process in tons/yr. Assume that the specific gravity of the acidic wastewater stream is 1.05.

- *10.28 Nitric acid (HNO_3) that is used industrially for a variety of reactions can be produced by the reaction of ammonia (NH_3) with air by the following overall reaction:

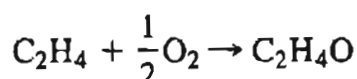


The product gas from such a reactor has the following composition (on a water free basis):

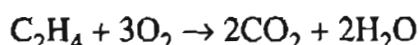
0.8% NH_3
9.5% HNO_3
3.8% O_2
85.9% N_2

Determine the percent conversion of NH_3 and the percent excess air used.

- *10.29 Ethylene oxide ($\text{C}_2\text{H}_4\text{O}$) is a high volume chemical intermediate that is used to produce glycol and polyethylene glycol. Ethylene oxide is produced by the partial oxidation of ethylene (C_2H_4) using a solid catalyst in a fixed-bed reactor:



In addition, a portion of the ethylene reacts completely to CO_2 and H_2O :



The product gas leaving a fixed-bed ethylene oxide reactor has the following water free composition: 20.5% $\text{C}_2\text{H}_4\text{O}$; 72.7% N_2 ; 2.3% O_2 ; and 4.5% CO_2 . Determine the percent excess air based in the desired reaction, and the lb/h of ethylene feed required to produce 100,000 ton/yr of ethylene oxide.

- **10.30 Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and ammonia form a sterile solution (no live cells) fed continuously into a vessel. Assume complete reaction. One product formed from the reaction contains ethanol, cells ($\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2}$), and water. The gas produced is CO_2 . If the reaction occurs anerobically (without the presence of oxygen), what is the minimum amount in kg of feed (ammonia and glucose) required to produce 4.6 kg of ethanol? Only 60% of the moles of glucose are converted to ethanol. The remainder is converted to cell mass, carbon dioxide, and water.
- *10.31 Refer to Example 10.9. Suppose that during combustion a very small amount (0.24%) of the entering nitrogen reacts with oxygen to form nitrogen oxides (NO_x). Also, suppose that the CO produced is 0.18% and the SO_2 is 1.4% of the $\text{CO}_2 + \text{SO}_2$ in the flue gas. The emissions listed by the EPA in the load units (ELU)/kg of gas are:

NO_x	0.22
CO	0.27
CO_2	0.09
SO_2	0.10

What is the total ELU for the stack gas? Note: The ELU are additive.

CHAPTER 11

MATERIAL BALANCE PROBLEMS INVOLVING MULTIPLE UNITS

Your objectives in studying this chapter are to be able to:

1. Write a set of independent material balances for a process involving more than one unit.
2. Solve problems involving several serially connected units.

If you have driven past an industrial plant, power station, or waste disposal facility, you must have noticed how complex the equipment is. Such plants involve a large number of interconnected processing units. Based on what you have learned in Chapters 6–10, are you now prepared to solve problems involving an entire plant? If not, study this chapter to find out what to do.

Looking Ahead

In this chapter we are going to discuss how to treat and solve material balance problems for systems of serially coupled units. You will be pleased to learn that principles employed in previous chapters still apply. All you have to do is apply them to individual subsystems and/or to the overall system.

Main Concepts

*There are nine and sixty ways of constructing tribal lays,
and every one of them is right.*

Kipling

A **process flowsheet (flowchart)** is a graphical representation of a process. A flowsheet describes the actual process in sufficient detail that you can use it to formulate material (and energy) balances. Flowsheets are also used for troubleshooting, control of operating conditions, and optimization of process performance. You will find that flowsheets are also prepared to represent proposed processes that involve new techniques or modifications of existing processes.

Figure 11.1 is a picture of a section of a plant. Figure 11.2a is a flowsheet of the process indicating the equipment sequence and the flow of materials.

Figure 11.2b is a **block diagram** corresponding to Figure 11.2a. The units appear as simple boxes called **subsystems** rather than as the more elaborate portrayal in Figure 11.2a. You should note that the operations of mixing and splitting are clearly denoted by boxes in Figure 11.2b, whereas the same functions appear only as intersecting lines in Figure 11.2a.

Figure 11.3a illustrates a *serial* combination of mixing and splitting stages.

In a **mixer**, two or more entering streams of different compositions are combined. In a **splitter**, two or more streams exit, all of which *have the same composition*. In a **separator**, the exit streams can be of different compositions.

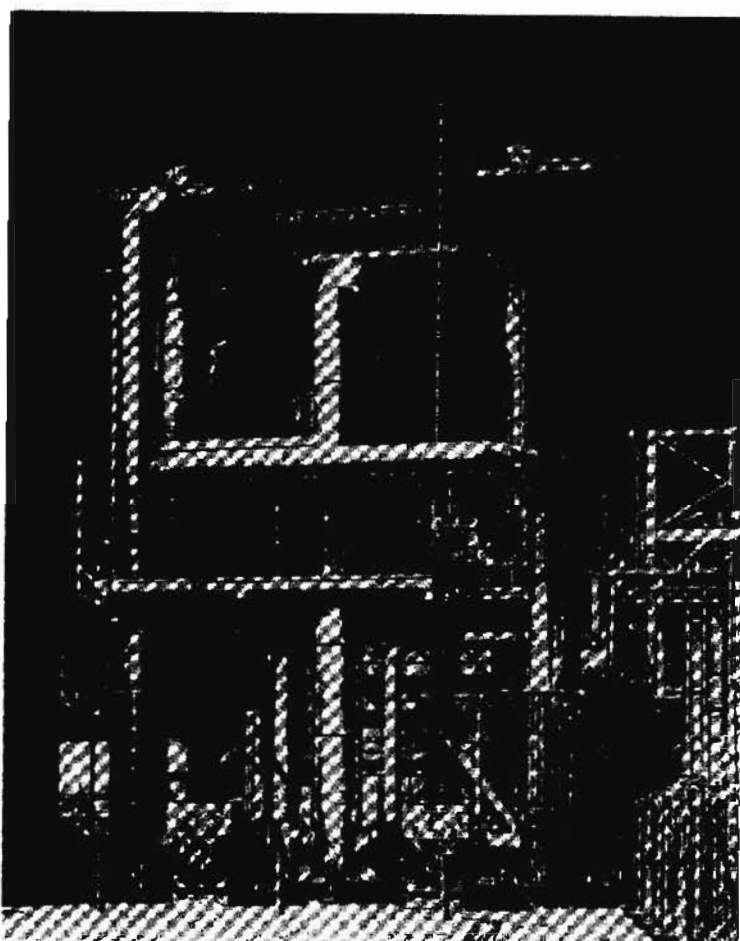
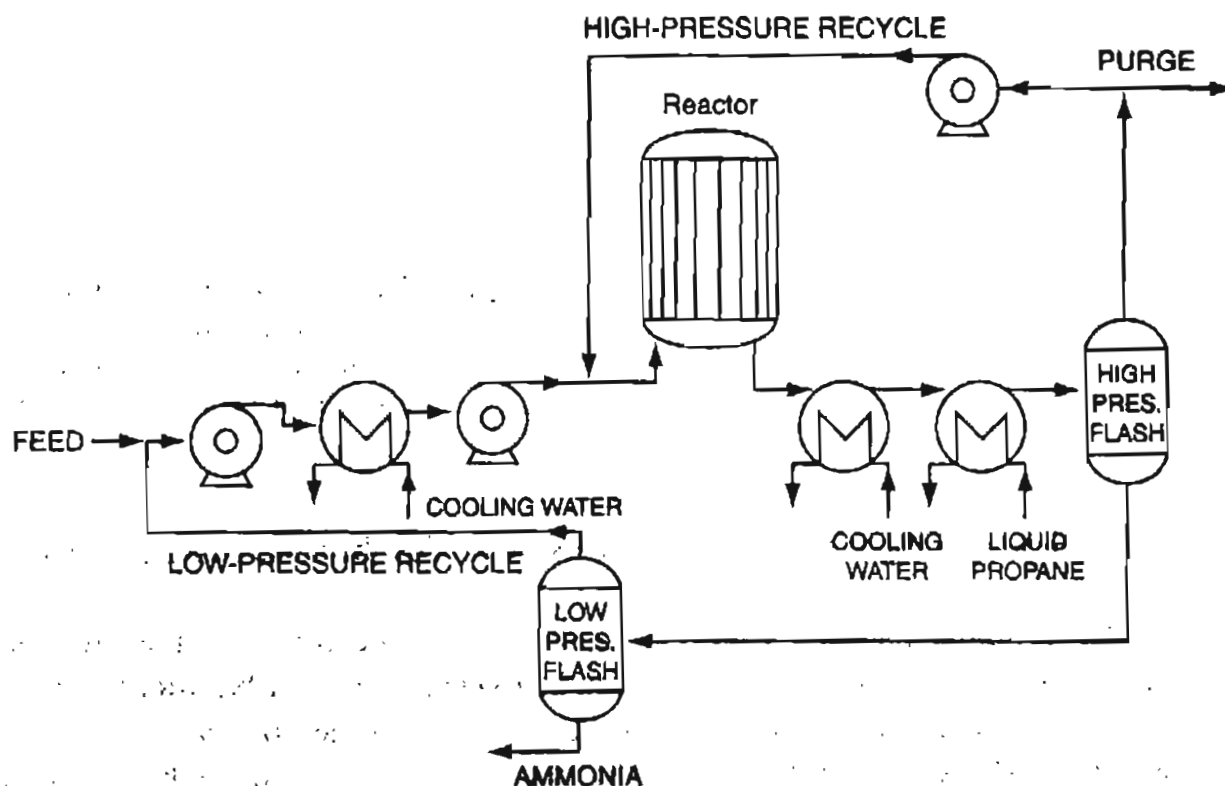
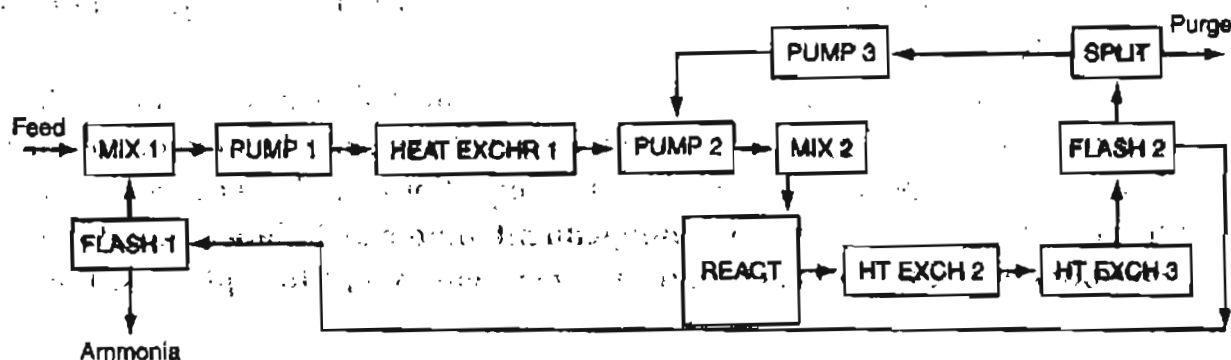


Figure 11.1 Section of a large ammonia plant showing the equipment in place.



a.



b.

Figure 11.2 (a) Flowsheet of the ammonia plant that includes major pieces of equipment and the materials flow. (b) Block diagram of the information flow corresponding to Figure 11.2a.

Examine Figure 11.3a. Which streams must have the same composition? Is the composition of stream 5 the same as the composition inside the unit represented by the box? It will be the same if the contents of the unit are **well mixed**, the usual assumption in this text. If no reaction takes place in the unit, the output composition in stream 5 is the properly weighted average of the input compositions 3 and 4. Do

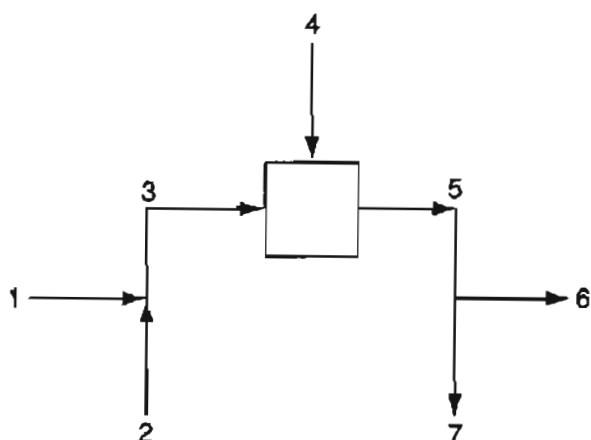


Figure 11.3a Serial mixing and splitting in a system without reaction. Streams 1 plus 2 mix to form Stream 3, and Stream 5 is split into Streams 6 and 7.

streams 5, 6, and 7 have the same composition? Yes, because streams 6 and 7 flow from a splitter fed by stream 5.

How many material balances can you formulate for the three process units shown in Figure 11.3a? First, you can make **overall material balances**, namely balances on a system that includes all of the units within the boundary denoted by the dashed line shown as I in Figure 11.3b. In addition, you can make balances on each of the three units that make up the overall process, as denoted by the boundaries defined by the dashed lines II, III, and IV in Figure 11.3c. Finally, you can make balances about combinations of two or more units simultaneously, as indicated by the boundaries defined by the dashed lines V, VI, and VII in Figures 11.3d to 11.3f, respectively.

You can conclude for the three process units shown in Figure 11.3a that you can make material balances on seven different systems. The important question is: How many independent material balance equations can be written for the process? In general, you can write **an independent material balance equation for each component present in each unit or subsystem except for splitters. For splitters,**

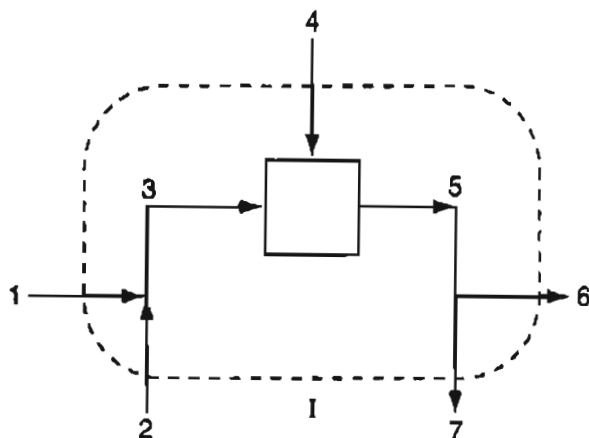


Figure 11.3b The dashed line I designates the boundary for overall material balances made on the process in Figure 11.3a.

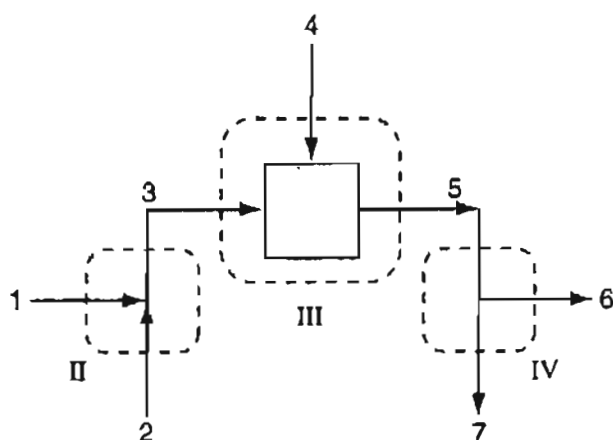


Figure 11.3c Dashed lines II, III, and IV designate the boundaries for material balances around each of the individual units comprising the overall process.

only one independent mass balance equation can be written regardless of the number of components present in the streams.

As an example, let's count the material balances that might be made for the process shown in Figure 11.3a. For the process shown in Figure 11.3a, assume that 3 components are present in the mixer, and four components present in the unit portrayed by the box. How many independent material balances can you write for the process with these assumptions? Did you get 8? Here is the count: mixer: 3, box: 4, splitter: 1, for a total of 8. Next, how many different material balances can you write in total for the process including both independent and dependent equations. You can make five overall balances (one for each component and the total balance) plus a total of 14 material balances for single units and 15 material balances for pairs of units. Therefore, you can write a total of 34 material balances of which only 8 are independent.

For this example, which 8 of the 34 possible material balance equations should you select? Certainly **you should select an independent set of equations**. As an example of what not to do, do not select a component balance for a particular compo-

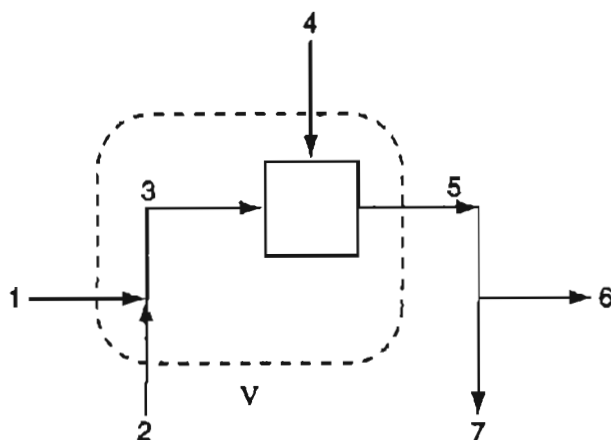


Figure 11.3d The dashed line V designates the boundary for material balances around a system comprised of the mixing point plus the unit portrayed by the box.

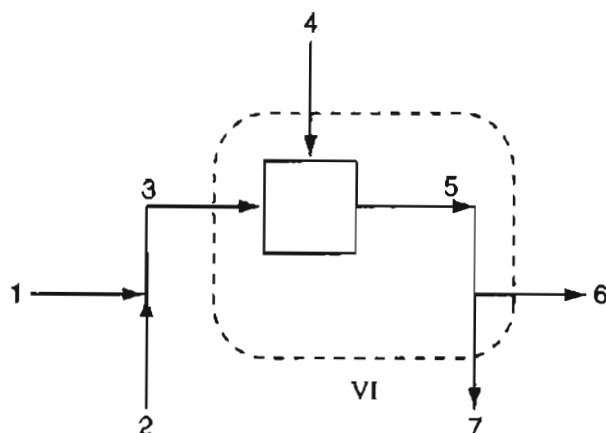


Figure 11.3e The dashed line VI designates the boundary for material balances about a system comprised of the unit portrayed by the box plus the splitter.

nent for each of the individual units in the process plus an overall balance for the same component. This set of equations would not be independent because, as you know, the overall balance for each species is just the sum of the respective species balances for the individual unit. As another example, don't use material balances for the total flow either overall or for an individual unit together with all of the respective species balances for the system.

What strategy should you use to select the particular unit or subsystem with which to start formulating your independent equations for a process comprised of a sequence of connected units? A good, but time-consuming, way to decide is to determine the degrees of freedom for various subsystems (single units or combinations of units) selected by inspection. A subsystem with zero degrees of freedom is a good starting point. Frequently, the best way to start is to make material balances for the **overall process**, ignoring information about the internal **connections**. If you ignore all of the internal streams and variables within a set of connected subsystems, you can treat the overall system exactly as you treated a single system in Chapters 7 through 10 by drawing a boundary about the entire set of subsystems as in Figure 11.3b.

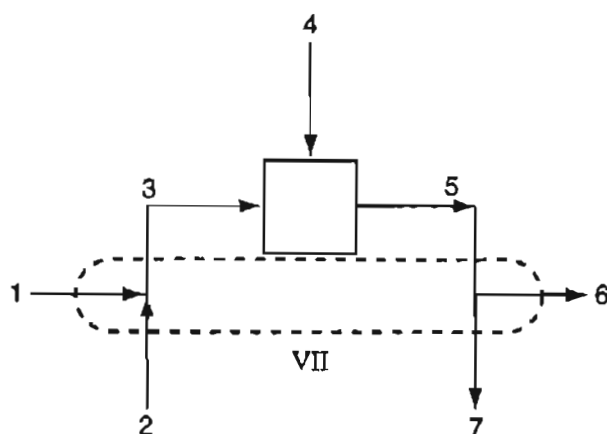


Figure 11.3f The dashed line VII designates the boundary for material balances about a system comprised of the mixer plus the splitter.

EXAMPLE 11.1 Determination of the Number of Independent Material Balances in a Process with Multiple Units

Examine Figure E11.1. No reaction takes place. The system is open and steady state. The arrows designate flows. The composition of each stream is as follows:

- (1) Pure A
- (2) Pure B
- (3) A and B, concentrations known: $\omega_A = 0.800$, $\omega_B = 0.200$
- (4) Pure C
- (5) A, B, and C, concentrations known: $\omega_A = 0.571$, $\omega_B = 0.143$, $\omega_C = 0.286$
- (6) Pure D
- (7) A and D, concentrations known: $\omega_A = 0.714$, $\omega_D = 0.286$
- (8) B and C, concentrations known: $\omega_B = 0.333$, $\omega_C = 0.667$

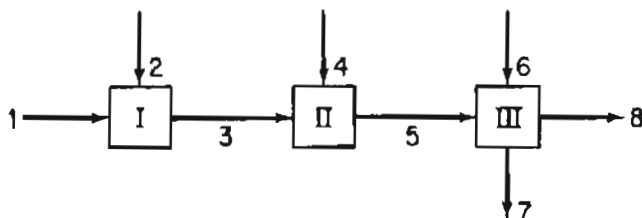


Figure E11.1

What is the maximum number of independent mass balances that can be generated to solve this problem? Write down the possible equations. Do they form a unique set?

Solution

Select each of the three units as a system. With respect to the material balances for the individual units, you can make 9 species equations as follows for the three units (ignoring any total balances for the 3 units, plus overall species and total balance, plus balances for combinations of units):

	Total number of species balances
At unit I, two species are involved	2
At unit II, three species are involved	3
At unit III, four species are involved	4
Total	9

However, not all of the balances are independent. In the following list, all of the known concentrations have been inserted, and F represents the stream flow designated by the superscript.

Subsystem I

$$\text{Balances } \begin{cases} A: F^1(1.00) + F^2(0) = F^3(0.800) & (a) \\ B: F^1(0) + F^2(1.00) = F^3(0.20) & (b) \end{cases}$$

Subsystem II

$$\text{Balances } \begin{cases} A: F^3(0.800) + F^4(0) = F^5(0.571) & (c) \\ B: F^3(0.200) + F^4(0) = F^5(0.143) & (d) \\ C: F^3(0) + F^4(1.00) = F^5(0.286) & (e) \end{cases}$$

Subsystem III

$$\text{Balances } \begin{cases} A: F^5(0.571) + F^6(0) = F^7(0.714) + F^8(0) & (f) \\ B: F^5(0.143) + F^6(0) = F^7(0) + F^8(0.333) & (g) \\ C: F^5(0.286) + F^6(0) = F^7(0) + F^8(0.667) & (h) \\ D: F^5(0) + F^6(1.00) = F^7(0.286) + F^8(0) & (i) \end{cases}$$

If you take as a basis $F^1 = 100$, seven values of F^i are unknown, hence only seven independent equations need to be written. Can you recognize by inspection that among the entire set of 9 equations two are redundant, and hence a unique solution can be obtained using 7 independent equations?

If you solved the 9 equations *sequentially* starting with Equation (a) and ending with Equation (i), along the way you would notice that Equation (d) is redundant with Equation (c) and Equation (h) is redundant with Equation (g). The redundancy of Equations (c) and (d) becomes apparent if you recall that the sum of the mass fractions in a stream is unity, hence an implicit relation exists between Equations (c) and (d) so that they are not independent. Why are Equations (g) and (h) not independent?

If you inspect the set of Equations (a) through (i) from the viewpoint of solving them sequentially, you will find that each one can be solved for one variable. Look at the following list:

Equation	Determines	Equation	Determines
(a)	F_3	(e)	F_4
(b)	F_2	(f)	F_7
(c)	F_5	(g)	F_8
(d)	F_5	(h)	F_8
		(i)	F_6

If you entered Equations (a) through (i) into a software program that solves equations, you would receive an error notice of some type because they are not an independent set of equations.

"If the fresh facts which come to our knowledge all fit themselves into the scheme, then our hypothesis may gradually become a solution."

Sherlock Holmes in Sir Arthur Conan Doyle's *The Complete Sherlock Holmes*, "The Adventure of Wisteria Lodge"

If you make one or more component material balances around the combination of subsystems I plus II, or II plus III or I plus III in Example 11.1, or around the entire set of three units, no additional *independent* material balances will be generated. Can you substitute one of the indicated alternative mass balances for an independent species mass balance? Yes (as long as the precision of the balance is about the same), unless it causes the equation set to be no longer independent.

In calculating the degrees of freedom for problems involving multiple units, you must be careful to involve only independent material balances and not miss any essential unknowns. All the same principles apply to processes with multiple units that were discussed in Chapters 7 through 10. Table 11.1 is a simplified checklist to help keep in mind possible unknowns and equations for a process.

Formal preparation of the entries in such a list will help you to identify which variables and equations to employ in solving for the unknowns, and, of course, to ensure that the degrees of freedom are zero before starting to solve the set of equa-

TABLE 11.1 Checklist of Variables and Equations to Consider in a Degree-of-Freedom Analysis

Variables

Flow variables:

- Species (or total flow) entering and leaving for each subsystem
- Species (or total flow) entering and leaving the overall system

Reaction variables:

- Extents of reaction (if any) in the minimal set for each subsystem

Equations

Basis for each subsystem or the overall system

Material balances (species or element):

- For each species or element (or their total) in each subsystem
- For each species or element (or their total) in the overall system

Specifications (for each subsystem and overall)

- Specified compositions
- Specified flow rates
- Specified flow ratios
- Specified conversions or extents of reaction
- Splitter restrictions

Implicit equations (sum of mole or mass fractions)

tions. Chapter 30 is a detailed discussion of determining the degrees of freedom for a complicated process.

*The solution goes on famously; but just as we have
got rid of the other unknowns, behold! V disappears
as well, and we are left with the indisputable but
irritating conclusion*

$$0 = 0$$

*This is a favorite device that mathematical equations
resort to, when we propound stupid questions.*

Sir Arthur Eddington

Frequently Asked Questions

1. In carrying out a degree-of-freedom analysis, do you have to include at the start of the analysis every one of the variables and equations that are involved in the entire process?

No. What you do is pick a system for analysis, and then you have to take into account only the unknowns and equations pertaining to the streams cut by the system boundary (plus those inside the system if it is an unsteady state system). For example, note in Example 11.1 that each subsystem was treated independently. If you had picked as the system the combination of all three of the units, then only the variables and equations pertaining to streams 1, 2, 4, 6, 7, and 8 would be involved in the analysis.

2. Should you use element material balances or species material balances in solving problems that involve multiple units?

For processes that do not involve reaction, use species balances. Element balances will involve redundancy and prove to be quite inefficient. For processes that do involve reaction, if you are given the reaction equations and information that will enable you to calculate the extent of reaction, species balances are easy to use. (If you are not specifically given the reaction equations, sometimes you can formulate them based on your experience, such as C burning with O_2 to yield CO_2 .) Otherwise use element balances. Just make sure that they are independent equations.

3. Do you have to understand the details of the elements of equipment in a plant in order to make material balances?

No. Collections of elements comprising a unit of equipment can be deemed to be the system. In fact, the balances do not have to represent any specific physical element of a unit. For convenience in analysis, a hypothetical system may be designated that has no corresponding physical presence. For example, the reactor in Figure 11.2a might be represented as a connected sequence of hypothetical individual reaction systems even though the inside of the reactor forms a continuous bed of catalyst.

We next look at some examples of making and solving material balances for systems composed of multiple units.

Example 11.2 Material Balances for Multiple Units in Which No Reaction Occurs

Acetone is used in the manufacture of many chemicals and also as a solvent. In its latter role, many restrictions are placed on the release of acetone vapor to the environment. You are asked to design an acetone recovery system having the flow-sheet illustrated in Figure E11.2. All the concentrations shown in E11.2 of both the gases and liquids are specified in *weight percent* in this special case to make the calculations simpler. Calculate, A , F , W , B , and D per hour. $G = 1400$ kg/hr.

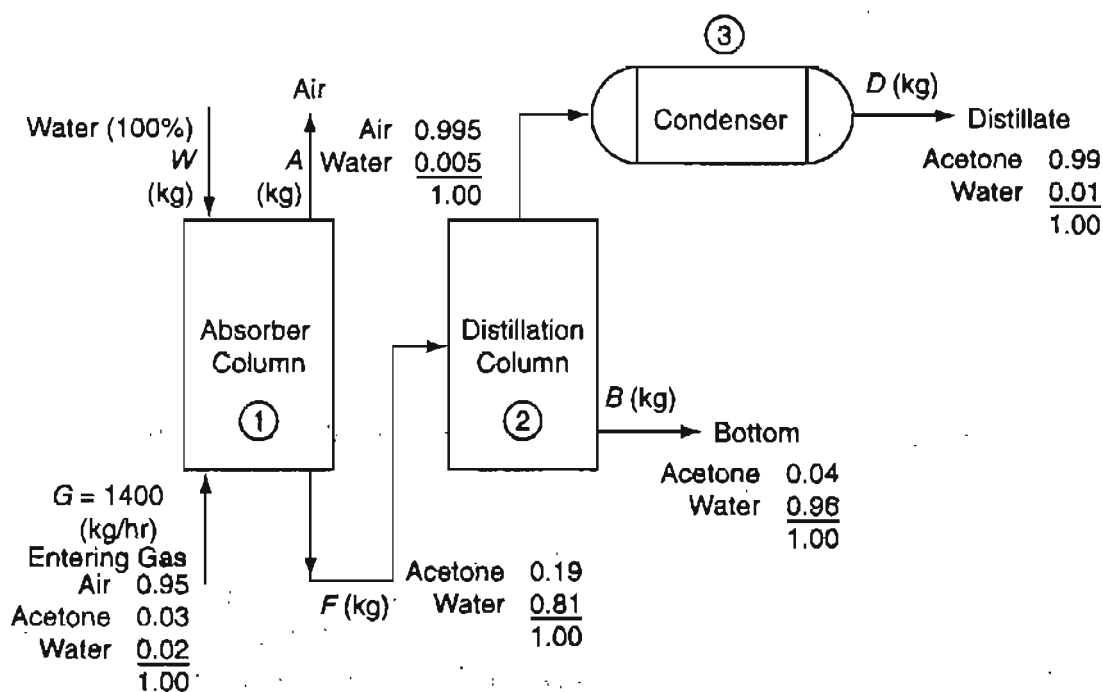


Figure E11.2

Solution

This is an open, steady-state process without reaction. Three subsystems exist.

Steps 1, 2, 3, and 4

All the stream compositions are given. All of the unknown stream flows are designated by letter symbols in the figure.

Step 5

Pick 1 hr as a basis so that $G = 1400$ kg.

Steps 6 and 7

We could start the analysis of the degrees of freedom with overall balances, but since the subsystems are connected serially, we will start the analysis with the absorber column, Unit 1, and then proceed to Unit 2, and then to Unit 3.

Unit 1 (Absorber)

Variables: 16

W, G, F, A (4 flow streams); species mass fractions in each stream = 3

so that $3 \times 4 = 12$ more variables

Equations: 16

Basis: G

Species material balances: 3 (one for each species)

Specifications: 12

$$\omega_A^G, \omega_{AC}^G, \omega_W^G$$

$$\omega_A^W = \omega_{AC}^W = 0, \omega_W^W = 1.00$$

$$\omega_A^A, \omega_W^A \text{ and } \omega_{AC}^A = 0$$

$$\omega_{AC}^F, \omega_W^F, \text{ and } \omega_A^F = 0$$

Implicit equations (such as $\sum \omega_i = 1$): all redundant given the specifications

Degrees of freedom: 0

Before proceeding to calculate the degrees of freedom for Unit 2 (the distillation column), you should note the complete lack of information about the properties of the stream going from the distillation column to Unit 3 (the condenser). In general it is best that you avoid making material balances on systems that include such streams, as they contain no useful information. Thus, the next system and degree-of-freedom analysis we select will be for the system composed of Units 2 and 3 combined.

Units 2 and 3 (Distillation Column plus Condenser)

Variables: 9

F, D, B (3 streams); species mass fractions in each stream = 2 so that $2 \times 3 = 6$ more variables

Equations: 9

Species material balances: 2 (one for each species)

Specifications: 6

$$\omega_{AC}^F, \omega_W^F, \omega_{AC}^D, \omega_W^D, \omega_{AC}^B, \omega_W^B$$

Implicit equations: all redundant

F is determined by first solving the equations for Unit 1
(the Absorber)

Degrees of freedom: 0 if F is known; 1 otherwise

What would happen if a correct analysis of the degrees of freedom for a subsystem gave +1? Then you would hope that the value for one of the unknowns in the subsystem could be determined from another subsystem in the overall system. In fact, for this Example, if you started the analysis of the degrees of freedom with the combined Units 2 plus 3, you would obtain a value of +1 because the value of F would not be known prior to solving the equations for Unit 1.

Step 8

The mass balances for Unit 1 after introduction of the basis and other specifications are as follows:

	<u>In</u>		<u>Out</u>	
Air:	1400 (0.95)	=	$A(0.995)$	(a)
Acetone:	1400 (0.03)	=	$F(0.19)$	(b)
Water:	$1400 (0.02) + W(1.00)$	=	$F(0.81) + A(0.005)$	(c)

(Check to make sure that the equations are independent.)

Step 9

Solve Equations (a), (b), and (c) via Polymath to get

$$A = 1336.7 \text{ kg/hr}$$

$$B = 221.05 \text{ kg/hr}$$

$$C = 157.7 \text{ kg/hr}$$

Step 10

(Check) Use the total balance.

$$\begin{array}{rcl}
 G + W & = & A + F \\
 1400 & & 1336 \\
 \underline{157.7} & & \underline{221.05} \\
 1557.7 & \equiv & 1557.1
 \end{array}$$

Step 8

The mass balances for the combined Units 2 plus 3 are:

$$\text{Acetone: } 221.05(0.19) = D(0.99) + B(0.04) \quad (d)$$

$$\text{Water: } 221.05(0.81) = D(0.01) + B(0.96) \quad (e)$$

Step 9

Solve Equations (d) and (e) simultaneously to get

$$D = 34.90 \text{ kg/hr}$$

$$B = 186.1 \text{ kg/hr}$$

Step 10

(Check) Use the total balance

$$F = D + B \text{ or } 221.05 \cong 34.90 + 186.1 = 221.0$$

As a matter of interest, what other mass balances could be written for the system and substituted for any one of the Equations (a) through (e)? Typical balances would be the overall balances

	<u>In</u>		<u>Out</u>	
Air:	$G(0.95)$	=	$A(0.995)$	(f)
Acetone:	$G(0.03)$	=	$D(0.99) + B(0.04)$	(g)
Water:	$G(0.02) + W$	=	$A(0.005) + D(0.01) + B(0.96)$	(h)
Total	$G + W$	=	$A + D + B$	(i)

Equations (f) through (i) do not add any extra information to the problem; the degrees of freedom are still zero. But any of the equations can be substituted for one of Equations (a) through (e) as long as you make sure that the resulting set of equations is independent.

Example 11.3 Material Balances for a Process Involving Multiple Units and Reactions

In the face of higher fuel costs and the uncertainty of the supply of a particular fuel, many companies operate two furnaces, one fired with natural gas and the other with fuel oil. In the RAMAD Corp., each furnace has its own supply of oxygen. The gas furnace uses air while the oil furnace uses an oxidation stream that analyzes: O₂, 20%; N₂, 76%; and CO₂, 4%. The stack gases go up a common stack. See Figure E11.3.

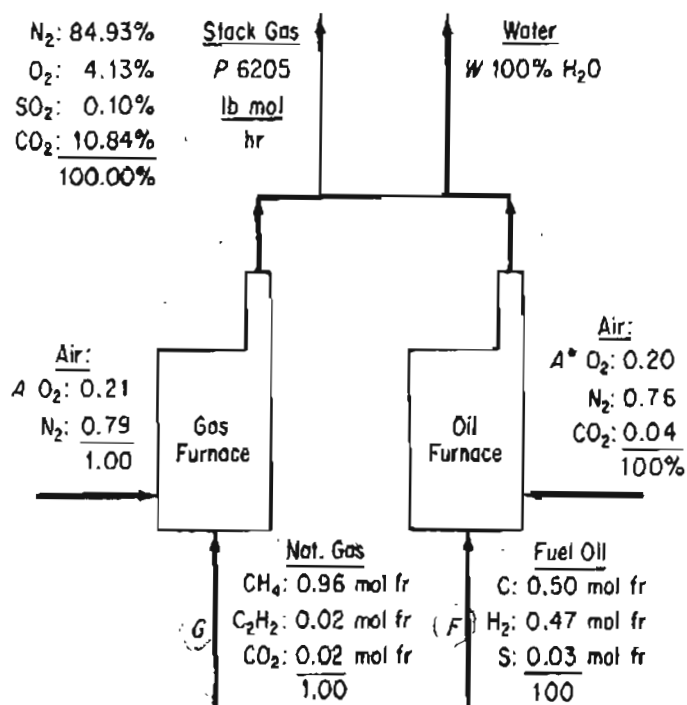


Figure E11.3

(Note that two outputs are shown from the common stack to point out that the stack gas analysis is on a dry basis but water vapor also exists. The fuel oil composition is given in mole fractions to save you the bother of converting mass fractions to mole fractions.)

During one blizzard, all transportation to the RAMAD Corp. was cut off, and officials were worried about the dwindling reserves of fuel oil because the natural gas supply was being used at its maximum rate possible. At that time, the reserve of fuel oil was only 560 bbl. How many hours could the company operate before shutting down if no additional fuel oil was attainable? How many lb mol/hr of natural gas were being consumed? The minimum heating load for the company when translated into the stack gas output was 6205 lb mol/hr of dry stack gas. Analysis of the fuels and stack gas at that time were:

Natural gas		Fuel oil (API gravity = 24.0) (Mol %)		Stack gas (Orsat analysis)	
CH ₄	96%	C	50	N ₂	84.93%
C ₂ H ₂	2%	H ₂	47	O ₂	4.13%
CO ₂	2%	S	3	CO ₂	10.84%
				SO ₂	0.10%

Also, calculate the percent increase in toxic emissions of arsenic and mercury per hour caused by the combustion of fuel oil rather than natural gas.

Data:

	Emission factors	
	Arsenic	Mercury
Natural gas	$2.30 \times 10^{-4} \text{ lb/10}^6 \text{ ft}^3$	$1.34 \times 10^{-4} \text{ lb/10}^6 \text{ ft}^3$
Oil	$3.96 \times 10^{-4} \text{ lb/10}^3 \text{ gal}$	$5.92 \times 10^{-4} \text{ lb/10}^3 \text{ gal}$

The molecular weight of the fuel oil was 7.91 lb/lb mol, and its density was 7.578 lb/gal.

Solution

This is an open, steady-state process with reaction. Two subsystems exist. We want to calculate F and G in lb mol/hr and then F in bbl/hr.

Steps 1, 2, 3, and 4

We will use elements for the material balances. The units of all the variables whose values are unknown will be pound moles. Rather than making balances for each furnace, since we do not have any information about the individual outlet streams of each furnace, we will make overall balances, and thus draw the system boundary around both furnaces.

Step 5

Basis: 1 hr, so that $P = 6205 \text{ lb mol}$

Steps 6 and 7

The simplified degree-of-freedom analysis is as follows. You have five elements in the problem and five streams whose values are unknown: A , G , F , A^* , and W ; hence, if the elemental mole balances are independent, you can obtain a unique solution for the problem.

Step 8

The overall balances for the elements are (in pound moles)

	<u>In</u>			<u>Out</u>	
2H:	$G(1.94)$	$+ F(0.47)$	=	$W(1)$	
2N:	$A(0.79)$	$+ A^*(0.76)$	=	$6205(0.8493)$	
2O:	$A(0.21)$	$+ A^*(0.20 + 0.04)$		$6205(0.0413 + 0.001 + 0.1084)$	
		$+ G(0.02)$	=		$+ W(1/2)$
S:	$F(0.03)$		=	$6205(0.0010)$	
C:	$G(0.96)$	$+ (2)(0.02) + 0.02$			
		$+ F(0.50) + 0.04A^*$	=	$6205(0.1084)$	

The balances can be shown to be independent.

Step 9

Solve the S balance for F (inaccuracy in the SO_2 concentrations will cause some error in F , unfortunately); the sulfur is a tie component. Then solve for the other four balances simultaneously for G . The results are:

$$F = 207 \text{ lb mol/hr}$$

$$G = 499 \text{ lb mol/hr}$$

Finally, the fuel oil consumption is

$$\frac{207 \text{ lb mol}}{\text{hr}} \left| \frac{7.91 \text{ lb}}{\text{lb mol}} \right| \frac{\text{gal}}{7.578 \text{ lb}} \left| \frac{\text{bbl}}{42 \text{ gal}} \right| = 5.14 \text{ bbl/hr}$$

If the fuel oil reserves were only 560 bbl, they could last at the most

$$\frac{560 \text{ bbl}}{5.14 \frac{\text{bbl}}{\text{hr}}} = 109 \text{ hr}$$

Basis: 1 hour

The arsenic and the mercury produced are:

Oil

$$(5.14 \text{ bbl/hr})(42 \text{ gal/bbl}) = 216 \text{ gal/hr}$$

$$\text{Arsenic: } \frac{216 \text{ gal}}{10^3 \text{ gal}} \left| \frac{3.96 \times 10^{-4} \text{ lb}}{10^3 \text{ gal}} \right| = 8.55 \times 10^{-5} \text{ lb}$$

$$\text{Mercury: } \frac{216 \text{ gal}}{10^3 \text{ gal}} \left| \frac{5.92 \times 10^{-4} \text{ lb}}{10^3 \text{ gal}} \right| = 12.78 \times 10^{-5} \text{ lb}$$

~~Natural Gas~~

$$(498 \text{ lb mol/hr})(359 \text{ ft}^3/\text{lb mol}) = 1.79 \times 10^5 \text{ ft}^3/\text{hr}$$

$$\text{Arsenic: } \frac{1.79 \times 10^5 \text{ ft}^3}{10^6 \text{ ft}^3} \left| \frac{2.30 \times 10^{-4} \text{ lb}}{10^6 \text{ ft}^3} \right| = 4.11 \times 10^{-5} \text{ lb}$$

$$\text{Mercury: } \frac{1.79 \times 10^5 \text{ ft}^3}{10^6 \text{ ft}^3} \left| \frac{1.34 \times 10^{-4} \text{ lb}}{10^6 \text{ ft}^3} \right| = 2.40 \times 10^{-5} \text{ lb}$$

The increase in levels of arsenic and mercury are:

$$\text{Arsenic: } \frac{(8.55 - 4.11) \times 10^{-5}}{4.11 \times 10^{-5}} (100) = 108\%$$

$$\text{Mercury: } \frac{(12.78 - 2.40) \times 10^{-5}}{2.40 \times 10^{-5}} (100) = 433\%$$

EXAMPLE 11.4 Analysis of a Sugar Recovery Process Involving Multiple Serial Units

Figure E11.4 shows the process and the known data. You are asked to calculate the compositions of every flow stream, and the fraction of the sugar in the cane that is recovered.

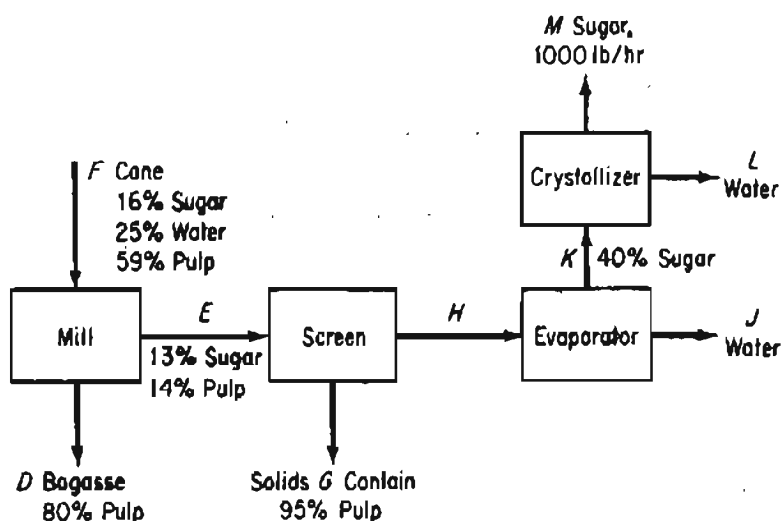


Figure E11.4

Solution

Steps 1, 2, 3, and 4

All of the known data have been placed on Figure E11.4. If you examine the figure, two questions naturally arise. What basis should you pick, and what system should you pick to start the analysis with? Some potential bases and systems lead to more equations to be solved simultaneously than others. You could pick as a basis $F = 100$ lb, $M = 1000$ lb (the same as 1 hour), or the value of any of the intermediate flow streams. You could pick an overall process as the system with which to start, or any of the individual units, or any consecutive combinations of units.

Step 5

Basis: 1 hour ($M = 1000$ lb)

Another important decision you must make is: what are the compositions of streams D , E , G , and H ? Stream F has three components, and presumably stream K contains only sugar and water. Does stream H contain pulp? Presumably not, because if you inspect the process flowsheet you will not find any pulp exiting anywhere downstream of the evaporator. Presumably streams D and G contain sugar and water because the problem implies that not all of the sugar in stream F is recovered. What happens if you assume streams D and G contain no water or no sugar?

Then you would write a set of material balances that are not independent and/or are inconsistent (have no solution). Try it.

Let S stand for sugar, P stand for pulp, and W stand for water.

Steps 6 and 7

Pick as the initial system the crystallizer. Why? Because (a) if you check the degrees of freedom for the crystallizer, only a small set of unknowns are involved with zero degrees of freedom, and (b) the crystallizer is at one end of the process. The unknowns are K , L , and ω_W^K . You can make two species balances, S and W , and know that $0.40 + \omega_W^K = 1$. Consequently, the degrees of freedom are zero, and the crystallizer seems to be a good system with which to start.

If you pick another basis, say $F = 100$ lb, and another system, say the mill, you would have 5 unknowns: D , E , ω_S^D , ω_W^D , and ω_W^E . You could make 3 species balances and employ two implicit equations, $\sum \omega_i^D = 1$ and $\sum \omega_i^E = 1$, hence the degrees of freedom are zero.

Steps 8 and 9

For the crystallizer the equations are (using $\omega_W^K = 1 - 0.40 = 0.60$)

$$\text{Sugar: } K(0.40) = L(0) + 1000$$

$$\text{Water: } K(0.60) = L + 0$$

from which you get $K = 2500$ lb and $L = 1500$ lb.

Step 10

Check using the total flows

$$2500 = 1500 + 1000 = 2500$$

The next stage in the solution is to pick the evaporator as the system, and repeat the degree-of-freedom analysis

$$3 \text{ variables: } H, J, \text{ and } \omega_W^H (\omega_P^H = 0)$$

3 equations: 2 independent species balances (the P balance is $0 = 0$), and

$$\sum \omega_i^H = 1$$

The degrees of freedom are zero. You can solve the equations, then proceed upstream one unit, solve the equations for the screen, and lastly solve the equations for the mill. The results for all of the variables are:

<i>lb</i>	<i>mass fraction</i>
$D = 16,755$	$\omega_S^D = 0.174$
$E = 7,819$	$\omega_W^D = 0.026$
$F = 24,574$	$\omega_W^E = 0.73$
$G = 1,152$	$\omega_S^G = 0.014$
$H = 6,667$	$\omega_W^G = 0.036$
$J = 4,167$	$\omega_W^H = 0.85$
$K = 2,500$	$\omega_W^K = 0.60$
$L = 1,500$	
$M = 1000$	

The fraction of sugar recovered is $[1000/(24,574)] (0.16) = 0.25$.

EXAMPLE 11.5 Production of a Hormone in Connected Reactors

Figure E 11.5 shows two different reactor configurations to produce a hormone.

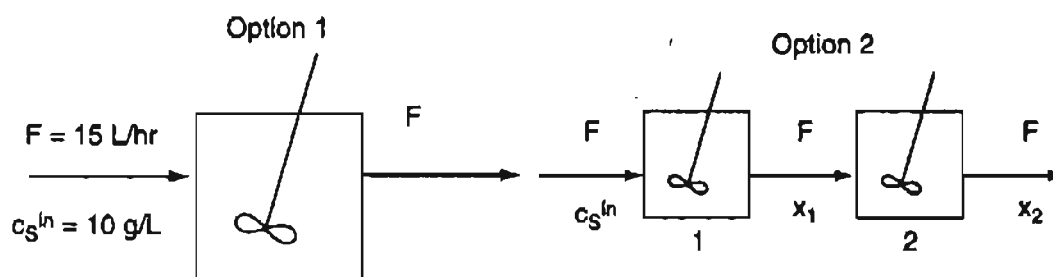


Figure E 11.5

The relation that gives the growth (generation in Equation (10.1)) of the hormone in each vessel in the steady state is the Monod equation

$$\mu = \frac{\mu_{\max} c_s}{K_s + c_s}$$

where μ = the specific growth rate, 1/hr

μ_{\max} = maximum specific growth rate (the state at which the concentration of nutrient becomes the limiting factor in the growth of cells), 1/hr

c_s = nutrient concentration in the vessel, g nutrient/L substrate

K_s = Monod constant, g nutrient/L substrate

The substrate is the liquid containing water, nutrients, and cells.

A coefficient that relates the g of dry cells formed/g nutrient consumed is usually given the symbol $Y_{x/s}$, and is called the biomass yield coefficient.

Two related processes for the growth of a hormone have been proposed. Option 1 is to use a single well mixed vessel having a volume of 100L. Option 2 is to use two well mixed vessels each of volume 50 L connected in series so that the output of vessel 1 becomes the input to vessel 2.

Which option will give the highest concentration (g cells/L of substrate)?

Data: The substrate flow rate into the vessel for Option 1, or into vessel 1 for Option 2, is 15 L/hr, and contains no cells, but contains a nutrient with a concentration of 10 g/L. $Y_{x/s}$ is equal to 0.2 g cells/g nutrient consumed. $K_s = 2$ g/L, and $\mu_{\max} = 0.4/\text{hr}$. The consumption of nutrient is $\mu x^{\text{out}}/Y_{x/s}$

Solution

Figure E11.5 shows the process stream information. Two material balances are involved in the solution to this problem. One balance is the cell balance. The concentration of cells will be denoted by x with the units of g cells/L. The other balance is the nutrient balance with c_s being the nutrient concentration. Because the vessels are well mixed, the concentration of cells and nutrient, respectively, in the effluent is the same as the concentration inside the vessel.

Assume each process is in the steady-state so that the accumulation in each vessel (the respective systems) is zero. We will use Equation (10.1) for the balances. The Monod equation applies to each vessel.

Option 1

$$\text{Cells} \quad 0 - \frac{F}{V}x^{\text{out}} + \mu x^{\text{out}} - 0 = 0 \quad (\text{a})$$

$$\text{Nutrient} \quad \frac{F}{V}c_s^{\text{in}} - \frac{F}{V}c_s^{\text{out}} + 0 - \frac{\mu x^{\text{out}}}{Y_{x/s}} = 0 \quad (\text{b})$$

In the literature of biotechnology the ratio F/V is termed the dilution rate, D , e.g., the number of culture volumes passing through the vessel per unit time, whereas in the chemical engineering literature the ratio V/F is known as the residence time.

$$\text{From Equation (a):} \quad \left(\frac{F}{V} - \mu\right)x^{\text{out}} = 0 \quad \text{hence} \quad \frac{F}{V} = \mu. \quad (\text{c})$$

$$\text{From Equation (b):} \quad \frac{F}{V}\left(c_s^{\text{in}} - c_s^{\text{out}} - \frac{x^{\text{out}}}{Y_{x/s}}\right) = 0$$

$$\text{hence} \quad x^{\text{out}} = Y_{x/s}(c_s^{\text{in}} - c_s^{\text{out}}) \quad (\text{d})$$

Next, introduce the values for the parameters into the equations. F/V is 15/100 per hour, and is equal to μ so that

$$\frac{15 \text{ L}}{1 \text{ hr}} \bigg| \frac{\quad}{100 \text{ L}} = \frac{0.4}{1 \text{ hr}} \bigg| \frac{c_s^{\text{out}} \text{ g/L}}{\frac{2 \text{ g}}{\text{L}} + \frac{c_s^{\text{out}}}{\text{L}}}$$

from which $c_s^{\text{out}} = 1.2 \text{ g nutrient/L substrate}$. Introduce this value into equation (d) to get

$$x^{\text{out}} = \frac{0.2 \text{ g cells}}{1 \text{ g nutrient consumed}} \bigg| \frac{\left(\frac{10 \text{ g nutrient}}{\text{L substrate}} - \frac{1.2 \text{ g nutrient}}{\text{L substrate}} \right)}{\quad} = 1.76 \text{ g cells/L substrate}$$

Option 2

The material balances are essentially the same as for Option except that the vessel volume is 50 L, and the output concentrations from vessel 1 become the input concentration to vessel 2. Thus, $F/V = (15 \text{ L/hr})/50 \text{ L} = 0.3/\text{hr}$.

For vessel 1:

$$\frac{15 \text{ L}}{\text{hr}} \bigg| \frac{\quad}{50 \text{ L}} = \frac{0.4 c_{s,1}^{\text{out}}}{2 + c_{s,1}^{\text{out}}}$$

hence $c_{s,1}^{\text{out}} = 6 \text{ g nutrient/L substrate}$. From equation (d)

$$x_1^{\text{out}} = 0.2 (10 - 6) = 0.8 \text{ g cells/L substrate}$$

For vessel 2:

Equation (a) now is

$$\frac{F}{V} x_1^{\text{out}} - \frac{F}{V} x_2^{\text{out}} + \mu x_2^{\text{out}} - 0 = 0 \quad (\text{e})$$

Equation (b) now is

$$\frac{F}{V} c_{s,1}^{\text{out}} - \frac{F}{V} c_{s,2}^{\text{out}} + 0 - \frac{\mu x_2^{\text{out}}}{Y_{x/s}} = 0 \quad (\text{f})$$

The solution of Equations (e), (f), plus the Monod equation (they form a non-linear set of equations) gives $c_{s,2}^{\text{out}} = 1.35 \text{ g nutrient/L substrate}$ and $x_2^{\text{out}} = 1.73 \text{ g cells/L substrate}$. In view of the number of significant figures in the values given for the data, the respective answers are essentially the same. How can you increase x^{out} ?

SELF-ASSESSMENT TEST

Questions

1. Can a system be comprised of more than one unit or piece of equipment?
2. Can one piece of equipment be treated as a set of several subsystems?
3. Does a flow sheet for a process have to show one subsystem for each process unit that is connected to one or more other process units?
4. If you count the degrees of freedom for each individual unit (subsystem) and add them up, can their total be different than the degrees of freedom for the overall system?

Problems

1. A two-stage separations unit is shown in Figure SAT11P1. Given that the input stream F1 is 1000 lb/hr, calculate the value of F2 and the composition of F2.

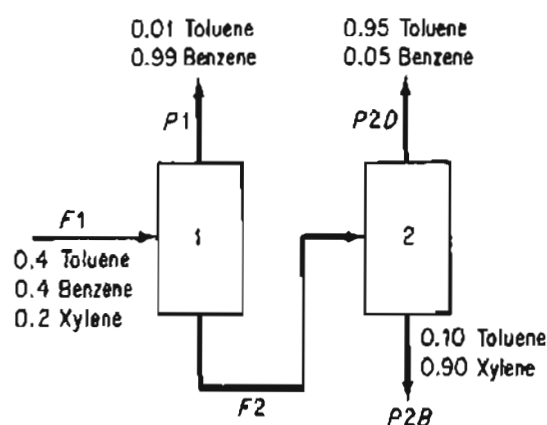


Figure SAT11P1

2. A simplified process for the production of SO_3 to be used in the manufacture of sulfuric acid is illustrated in Figure SAT11P2. Sulfur is burned with 100% excess air in the burner, but for the reaction $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$, only 90% conversion of the S to SO_2 is achieved in the burner. In the converter, the conversion of SO_2 to SO_3 is 95% complete. Calculate the kg of air required per 100 kg of sulfur burned, and the concentrations of the components in the exit gas from the burner and from the converter in mole fractions.

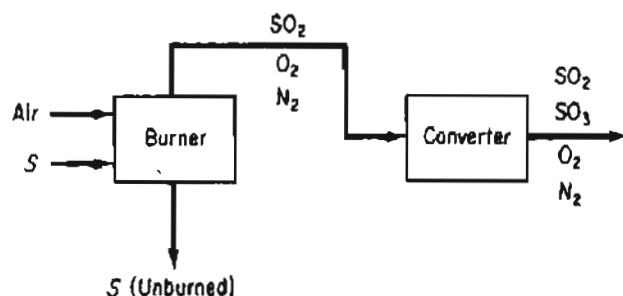
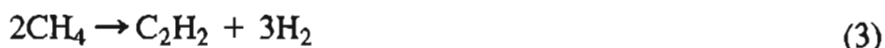


Figure SAT11P2

3. In the process for the production of pure acetylene, C_2H_2 (see Figure SAT11P3), pure methane (CH_4), and pure oxygen are combined in the burner, where the following reactions occur:



- Calculate the ratio of the moles of O_2 to moles of CH_4 fed to the burner.
- On the basis of 100 lb mol of gases leaving the condenser, calculate how many pounds of water are removed by the condenser.
- What is the overall percentage yield of product (pure) C_2H_2 , based on the carbon in the natural gas entering the burner?

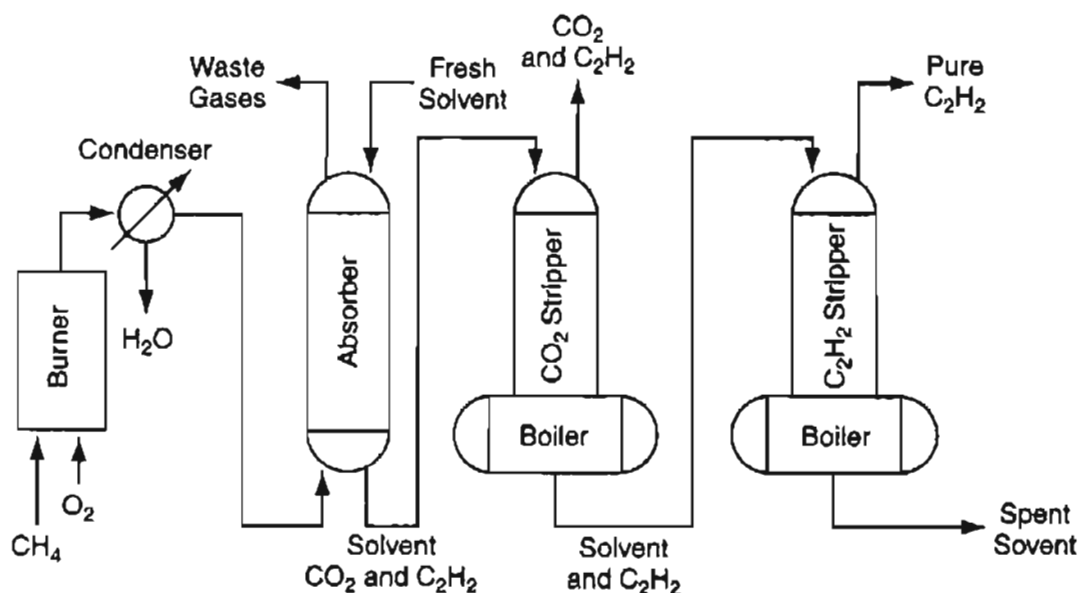


Figure SAT11P3

The gases from the burner are cooled in the condenser that removes all of the water. The analysis of the gases leaving the condenser is as follows:

	Mol %
C_2H_2	8.5
H_2	25.5
CO	58.3
CO_2	3.7
CH_4	4.0
Total	100.0

These gases are sent to an absorber where 97% of the C_2H_2 and essentially all the CO_2 are removed with the solvent. The solvent from the absorber is sent to the CO_2 stripper,

where all the CO_2 is removed. The analysis of the gas stream leaving the top of the CO_2 stripper is as follows:

	Mol %
C_2H_2	7.5
CO_2	92.5
Total	100.0

The solvent from the CO_2 stripper is pumped to the C_2H_2 stripper, which removes all the C_2H_2 as a pure product.

Thought Problem

1. When choosing a subsystem in a process for which to start making material balances, what criterion should you use in making the selection?

Discussion Problems

1. A household can be represented as a small process. Material (and energy as well) flows in and out. Prepare a flow diagram of a household that includes the kitchen, laundry, lavatory, toilets, bathtubs/showers, furnace, and air conditioners, and look up data so that you can estimate all of the material flows in and out of the system as well as recycle flows.
2. Look up the description of a process in an encyclopedia that includes a flow diagram of the process. Select the systems to be used in making material balances, and explain the reasons for your choices.

Looking Back

In this chapter you have seen how systems composed of more than one subsystem can be treated by the same principles that you used to treat single systems. Whether you use combinations of material balances from each of several subsystems or lump all of the units into one system, all you have to do is check to see that the number of independent equations you prepare is adequate to solve for the variables whose values are unknown. Flow sheets can help in the preparation of the equation set.

GLOSSARY OF NEW WORDS

Block diagram A sequence of boxes, circles, and so on used to represent operational features of the process flowsheet.

Connections Streams flowing between subsystems (units).

Flowchart A graphical representation of the process layout.

Mixer Apparatus to combine two or more flow streams.

Overall process The entire system composed of subsystems (units).

Process flowsheet A graphical representation of the process. See Flowchart.

Separator Apparatus that produces two or more streams of different composition from the fluid(s) entering the apparatus.

Splitter Apparatus that divides the flow into two or more streams of the same composition.

Subsystem A designated part of the complete system.

Well mixed Material within the system (equipment) is of uniform composition, and the exit stream(s) is of the same composition as the material inside the system.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent.

Baldea, M. "Dynamics and Control of Process Networks with Recycle and Purge," Paper 252 presented at AIChE meeting, Indianapolis, IN, November 4 (2002).

Nagiev, M. *The Theory of Recycle Processes in Chemical Engineering*. MacMillan, New York (1964).

PROBLEMS

- *11.1 For Figure P11.1 how many independent equations are obtained from the overall balance around the entire system plus the overall balances on units A and B? Assume that only one component exists in each stream.

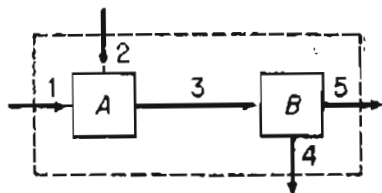
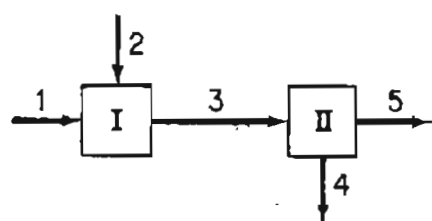


Figure P11.1

- *11.2 What is the maximum number of independent material balances that can be written for the process in Fig. P11.2?



Steam composition (known)

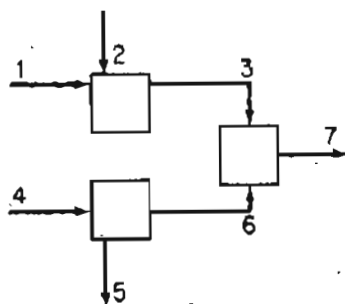
- | | |
|---|--------------------|
| 1 | Pure A |
| 2 | Pure B |
| 3 | Mixture of A and B |
| 4 | |
| 5 | |

Steam flows (unknown)

Figure P11.2

- **11.3 What is the maximum number of independent material balances that can be written for the process in Fig. P11.3? The stream flows are unknown.

Suppose you find out that A and B are always combined in each of the streams in the same ratio. How many independent equations could you write?

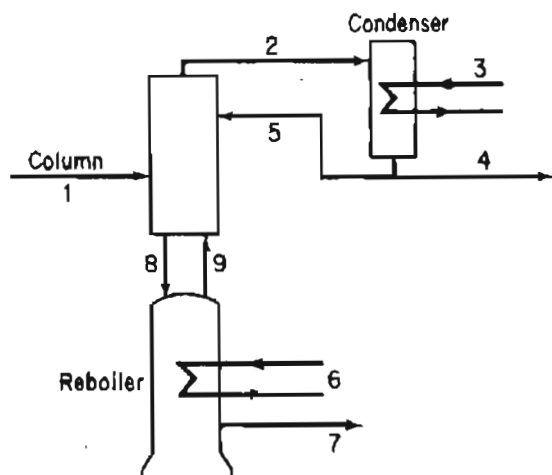


Steam composition (known)

- | | |
|---|----------------|
| 1 | A and B |
| 2 | Pure C |
| 3 | A, B, and C |
| 4 | D and E |
| 5 | Pure E |
| 6 | Pure D |
| 7 | A, B, C, and D |

Figure P11.3

- *11.4 The diagram in Figure P11.4 represents a typical but simplified distillation column. Streams 3 and 6 consist of steam and water, and do not come in contact with the fluids in the column that contains two components. Write the total and component material balances for the three sections of the column. How many independent equations would these balances represent? Assume that stream 1 contains n components.



- | | |
|---|--------------------------|
| 1 | Feed |
| 2 | Overhead |
| 3 | Cooling H ₂ O |
| 4 | Product |
| 5 | Reflux |
| 6 | Steam |
| 7 | Bottoms |
| 8 | Liquid flow to reboiler |
| 9 | Vapor flow to column |

Figure P11.4

- **11.5** A distillation process is shown in Figure P11.5. You are asked to solve for all the values of the stream flows and compositions. How many variables and unknowns are there in the system? How many independent material balance equations can you write? Explain each answer and show all details how you reached your decision. For each stream (except F , the only components that occur are labeled below the stream).

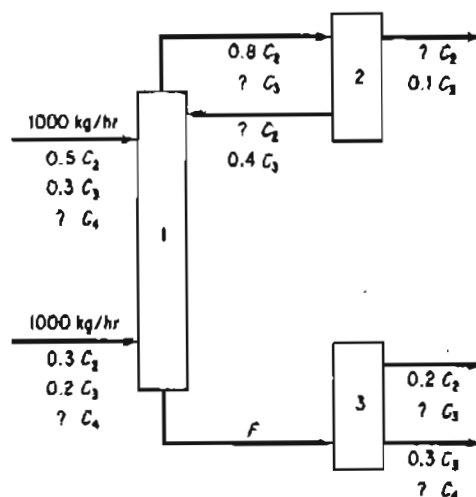


Figure P11.5

- ***11.6** In Figure P11.6 you will see two successive liquid separations columns operating in tandem in the steady state (and with no reaction taking place). The compositions of the feed and products are as shown in the figure. The amount of W_2 is 20% of the feed. Focus only on the material balances. Write down the names of the material balances for each column treated as separate units (one set for each column), along with the balances themselves placed next to the names of the balances. Also, place an asterisk in front of the names of the balances that will comprise a set of independent equations for each column. Write down in symbols the unknowns for each column. Calculate the degrees of freedom for each column separately.

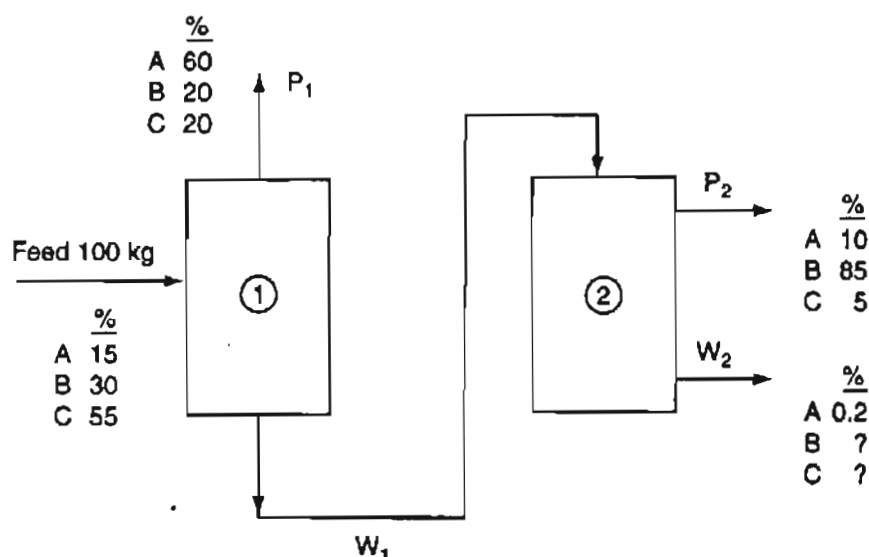


Figure P11.6

Then determine the number of independent equations for the overall system composed of the two columns together by listing the duplicate variables (by symbols) and unused specifications as well as the redundant equations, and appropriately adding or subtracting them from the values found in the first paragraph above. Determine the degrees of freedom for the overall system.

Check your results obtained in paragraph 2 above by repeating the entire analysis of independent equations, unknowns, and degrees of freedom for the overall system. Do they agree? They should.

Do not solve any of the equations in this problem.

***11.7** Examine Figure P11.7 provided through the courtesy of Professor Mike Cutlip.

- Calculate the molar flow rate of D_1 , D_2 , B_1 and B_2 .
- Reduce the feed flow rate for each one of the compounds by 1% in turn. Calculate the flow rates of D_1 , D_2 , B_1 and B_2 again. Do you notice something unusual? Explain your results.

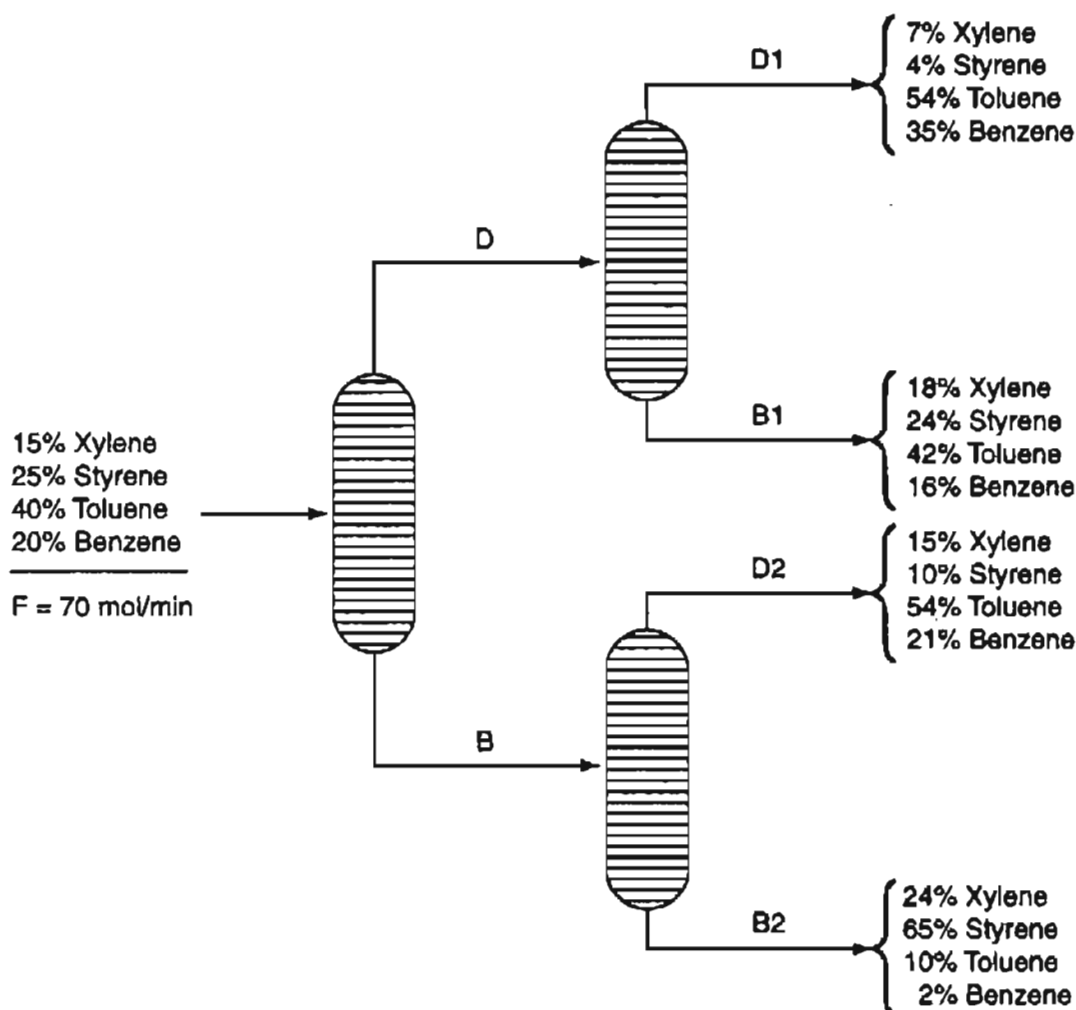


Figure P11.7

***11.8** Figure P11.8 shows a schematic for making fresh water from sea water by freezing. The pre-chilled sea water is sprayed into a vacuum at a low pressure. The cooling required to freeze some of the feed sea water comes from evaporation of a fraction of

the water entering the chamber. The concentration of the brine stream, B, is 4.8% salt. The pure salt-free water vapor is compressed and fed to a melter at a higher pressure where the heat of condensation of the vapor is removed through the heat of fusion of the ice which contains no salt. As a result, pure cold water and concentrated brine (6.9%) leave the process as products.

- (a) Determine the flow rates of streams W and D if the feed is 1000 kg per hour?
 (b) Determine the flow rates of streams C, B and A per hour?

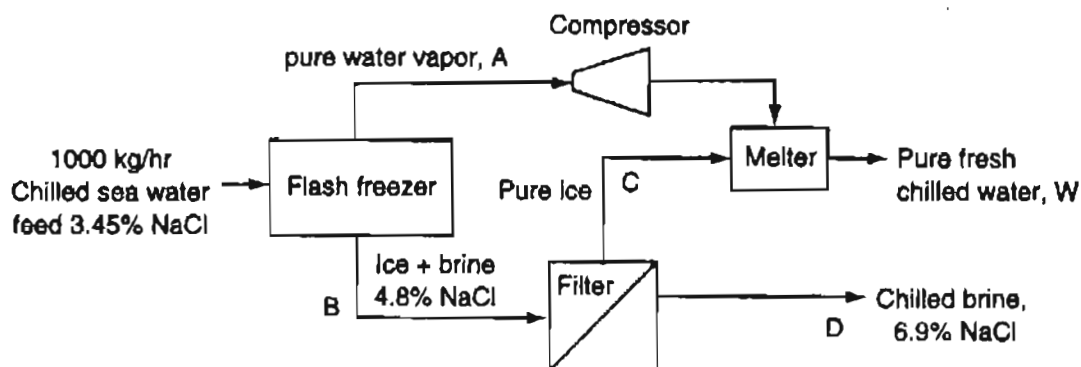


Figure P 11.8

- *11.9 Monoclonal antibodies are used to treat various diseases as well as in diagnostic tests. Figure P11.9 shows a typical process used to produce monoclonal antibodies. A stirred tank bioreactor grows the cells of the antibody of interest, namely immunoglobulin G (IgG). After fermentation in the reactor, a batch of 2200 L contains 220 grams of the product IgG. The batch is processed through a number of stages as shown in Figure P11.9 before the purified product is obtained. In the diafiltration stage, 95% of the IgG entering the filter is recovered, in the ultra filtration stage 95% of the entering IgG is recovered, and in the chromatography 90% is recovered.

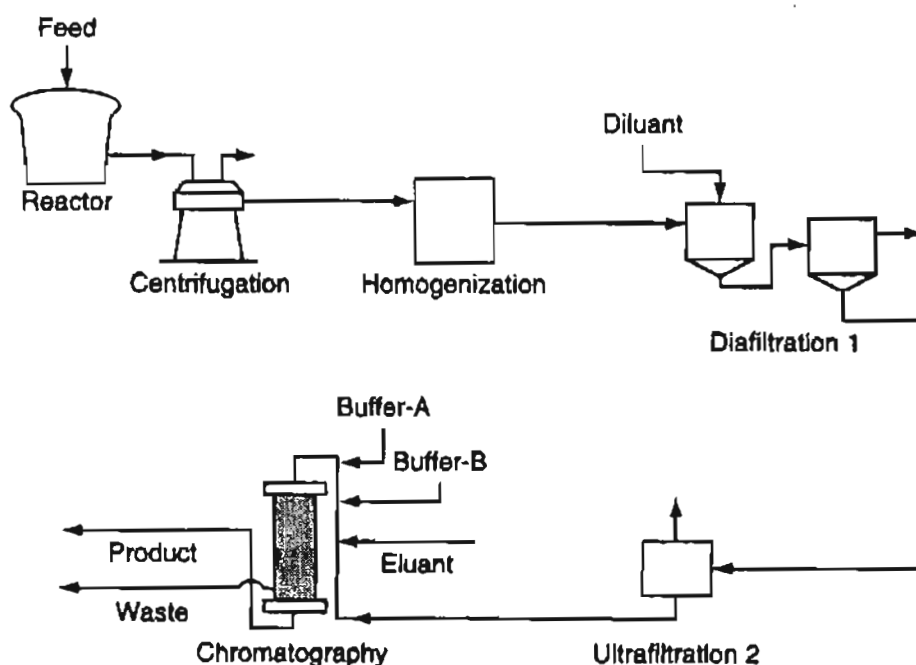


Figure P 11.9

TABLE P11.9

Component	Total Inlet	Total Outlet	Product
Ammonium Sulfate	64.69	64.69	
Biomass	0.00	0.87	
Glycerol	1.85	1.85	
IgG	0.00	0.22	0.14
Growth Media	21.76	8.41	
Na3Citrate	0.80	0.80	
Phosphoric Acid	1,040.96	1,040.96	
Sodium Hydrophosphate	6.83	6.81	
Sodium Chloride	55.18	55.19	
Sodium Hydroxide	6.83	6.81	
Tris-HCl	0.69	0.69	
Water	11,459.59	11,458.80	
Injection water	18,269.54	18,269.54	
Total	30,928.72	30,928.72	0.14

Table P11.9 lists the essential components entering and leaving the overall process in kg per batch. What is the fractional yield of the product IgG of the 220 g produced in the reactor?

- **11.10** Several streams are mixed as shown in Figure P11.10. Calculate the flows of each stream in kg/s.

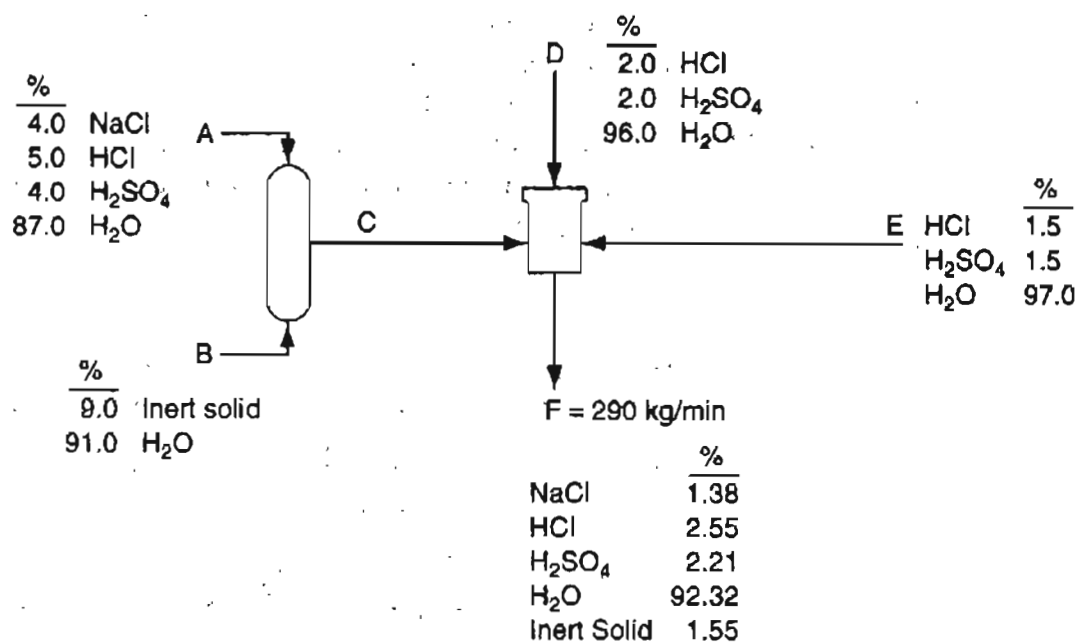


Figure P11.10

- ***11.11** In 1988, the U.S. Chemical Manufacturers Association (CMA) embarked upon an ambitious and comprehensive environmental improvement effort—the Responsible Care initiative. Responsible Care committed all of the 185 members of the CMA to ensure continual improvement in the areas of health, safety, and environmental qual-

ity, as well as in eliciting and responding to public concerns about their products and operations.

One of the best ways to reduce or eliminate hazardous waste is through source reduction. Generally, this means using different raw materials or redesigning the production process to eliminate the generation of hazardous byproducts. As an example, consider the following countercurrent extraction process (Figure P11.11) to recover xylene from a stream that contains 10% xylene and 90% solids by weight.

The stream from which xylene is to be extracted enters Unit 2 at a flow rate of 2000 kg/hr. To provide a solvent for the extraction, pure benzene is fed to Unit 1 at a flow rate of 1000 kg/hr. The mass fractions of the xylene in the solids stream (F) and the clear liquid stream (S) have the following relations: $10 \omega_{\text{Xylene}}^F = \omega_{\text{Xylene}}^S$ and $10 \omega_{\text{Xylene}}^{F^2} = \omega_{\text{Xylene}}^{S^1}$.

Determine the benzene and xylene concentrations in all of the streams. What is the percent recovery of the xylene entering the process at Unit 2?

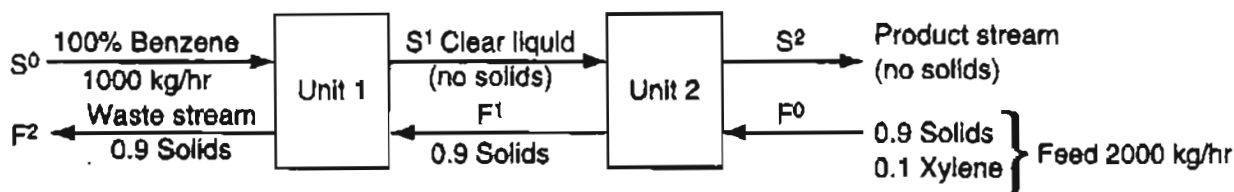


Figure P11.11

- **11.12** Figure P11.12 shows a three-stage separation process. The ratio of P_3/D_3 is 3, the ratio of P_2/D_2 is 1, and the ratio of A to B in stream P_2 is 4 to 1. Calculate the composition and percent of each component in stream E .

Hint: Although the problem comprises connected units, application of the standard strategy of problem solving will enable you to solve it without solving an excessive number of equations simultaneously.

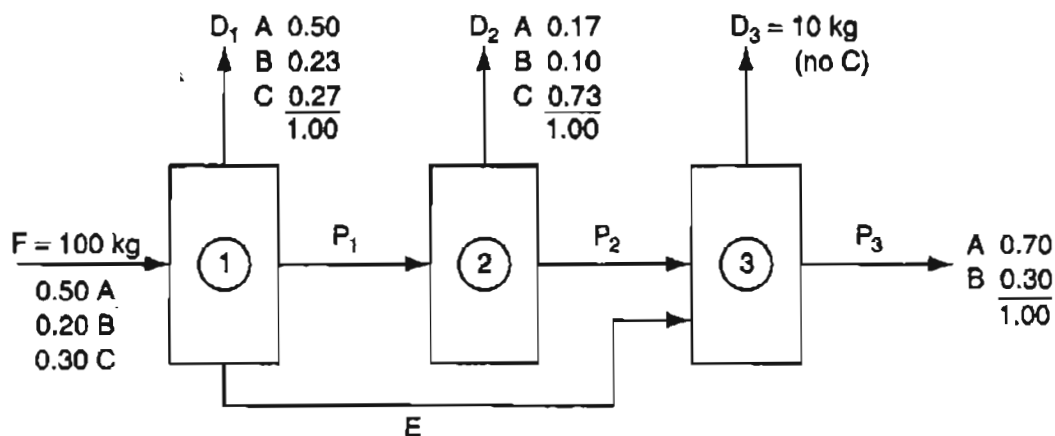


Figure P11.12

- *11.13** In a tissue paper machine (Figure P11.13), stream N contains 85% fiber. Find the unknown fiber values (all values in the figure are in kg) in kg for each stream.

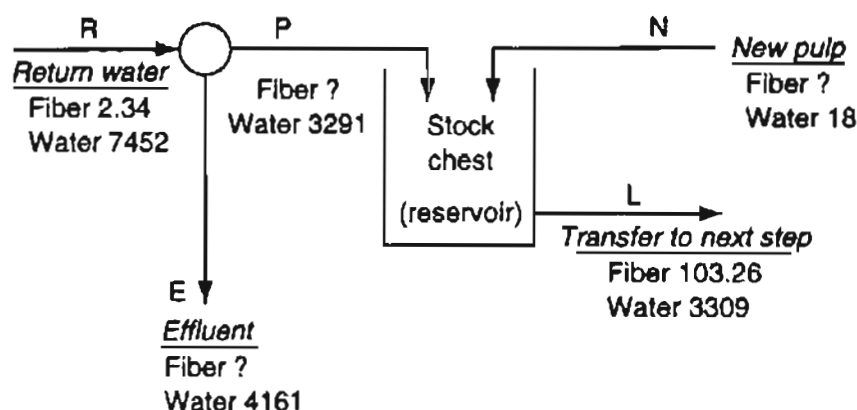


Figure P11.13

- **11.14** Metallurgical-grade silicon is purified to electronic grade for use in the semiconductor industry by chemically separating it from its impurities. The Si metal reacts in varying degrees with hydrogen chloride gas at 300°C to form several polychlorinated silanes. Trichlorosilane is liquid at room temperature and is easily separated by fractional distillation from the other gases. If 100 kg of silicon is reacted as shown in Figure P11.14, how much trichlorosilane is produced?

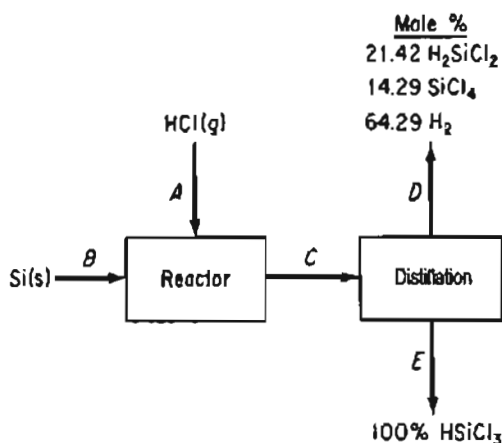


Figure P11.14

- ***11.15** A furnace burns fuel gas of the following composition: 70% Methane (CH_4), 20% Hydrogen (H_2) and 10% Ethane (C_2H_6) with excess air. An oxygen probe placed at the exit of the furnace reads 2% oxygen in the exit gases. The gases are passed then through a long duct to a heat exchanger. At the entrance to the heat exchanger the Orsat analysis of the gas reads 6% O_2 . Is the discrepancy due to the fact that the first analysis is on a wet basis and the second analysis on a dry basis (no water condenses in the duct), or due to an air leak in the duct?

If the former, give the Orsat analysis of the exit gas from the furnace. If the latter, calculate the amount of air that leaks into the duct per 100 mole of fuel gas burned.

- **11.16** A power company operates one of its boilers on natural gas and another on oil. The analyses of the fuels show 96% CH₄, 2% C₂H₂, and 2% CO₂ for the natural gas and C_nH_{1.8n} for the oil. The flue gases from both groups enter the same stack, and an Orsat analysis of this combined flue gas shows 10.0% CO₂, 0.63% CO, and 4.55% O₂. What percentage of the total carbon burned comes from the oil?
- **11.17** Sodium hydroxide is usually produced from common salt by electrolysis. The essential elements of the system are shown in Figure P11.17.
- What is the percent conversion of salt to sodium hydroxide?
 - How much chlorine gas is produced per pound of product?
 - Per pound of product, how much water must be evaporated in the evaporator?

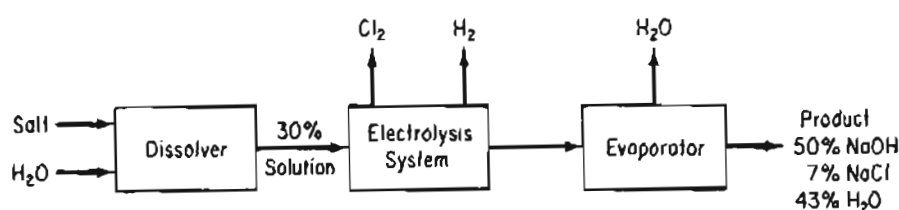
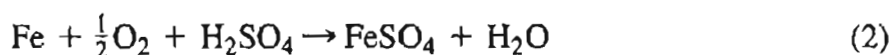


Figure P11.17

- ***11.18** The flowsheet shown in Fig. P11.18 represents the process for the production of titanium dioxide (TiO₂) used by Canadian Titanium Pigments at Varennes, Quebec. Sorel slag of the following analysis:

	Wt%
TiO ₂	70
Fe	8
Inert silicates	22

is fed to a digester and reacted with H₂SO₄, which enters as 67% by weight H₂SO₄ in a water solution. The reactions in the digester are as follows:



Both reactions are complete. The theoretically required amount of H₂SO₄ for the Sorel slag is fed. Pure oxygen is fed in the theoretical amount for all the Fe in the Sorel slag. Scrap iron (pure Fe) is added to the digester to reduce the formation of ferric sulfate to negligible amounts. Thirty-six pounds of scrap iron are added per pound of Sorel slag.

The products of the digester are sent to the clarifier, where all the inert silicates and unreacted Fe are removed. The solution of TiOSO₄ and FeSO₄ from the clarifier is cooled, crystallizing the FeSO₄, which is completely removed by a filter. The prod-

uct TiOSO_4 solution from the filter is evaporated down to a slurry that is 82% by weight TiOSO_4 .

The slurry is sent to a dryer from which a product of pure hydrate, $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$, is obtained. The hydrate crystals are sent to a direct-fired rotary kiln, where the pure TiO_2 is produced according to the following reaction:



Reaction (3) is complete.

On the basis of 100 lb of Sorel slag feed, calculate:

- The pounds of water removed by the evaporator.
- The exit lb of H_2O per lb dry air from the dryer if the air enters having 0.036 moles H_2O per mole dry air and the air rate is 18 lb mol of dry air per 100 lb of Sorel slag.
- The pounds of product TiO_2 produced.

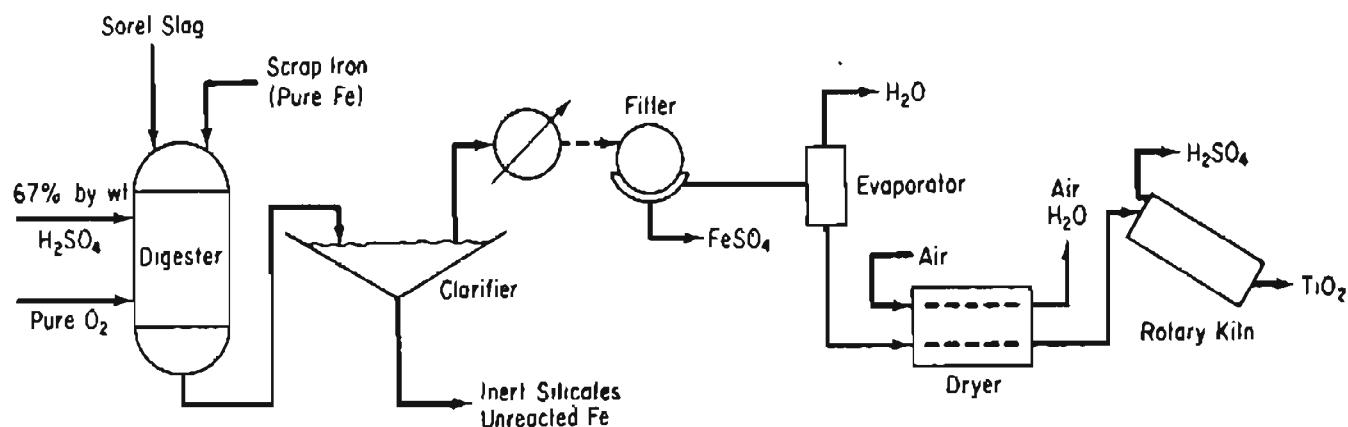


Figure P11.18

- *11.19** An enzyme is a protein that catalyzes a specific reaction, and its activity is reported in a quantity called "units". The specific activity is a measure of the purity of an enzyme. The fractional recovery of an enzyme can be calculated from the ratio of the specific activity (units per mg) after processing occurs to the initial specific activity. A three stage process for the purification of an enzyme involves
1. Breakup of the cells in a biomass to release the intercellular products.
 2. Separation of the enzyme from the intercellular product.
 3. Further separation of the enzyme from the output of stage 2.

Based on the following data for one batch of biomass, calculate the percent recovery of the enzyme after each of the three stages of the process. Also calculate the purification of the enzyme that is defined as the ratio of the specific activity to the initial specific activity. Fill in the blank columns of the following table.

Stage No.	Activity (units)	Protein present (mg)	Specific activity (units/mg)	Percent recovery	Purification
1	6860	76,200			
2	6800	2,200			
3	5300	267			

CHAPTER 12

RECYCLE, BYPASS, PURGE, AND THE INDUSTRIAL APPLICATION OF MATERIAL BALANCES

12.1 Introduction	342
12.2 Recycle without Chemical Reaction	347
12.3 Recycle with Chemical Reaction	355
12.4 Bypass and Purge	365
12.5 The Industrial Application of Material Balances	373

Your objectives in studying this chapter are to be able to:

1. Draw a flow diagram or sketch for problems involving recycle, bypass, and purge.
2. Apply the 10-step strategy to solve steady-state problems (with and without chemical reaction) involving recycle, bypass, and/or purge streams.
3. Solve problems involving a modest number of interconnected units by making appropriate balances.
4. Use the concepts of extent of reaction, overall conversion, and single-pass (once-through) conversion in solving recycle problems involving reactors.
5. Explain the purpose of a recycle stream, a bypass stream, and a purge stream.
6. Understand in a general sense how material balances are used in industry.

*I think that my friends would agree
How much recycle confuses me
It's something quite new
Only clear to a few
I'd rather be watching TV*

DMH

Looking Ahead

In this chapter we discuss material balances involving recycle—instances in which material from down stream of the process, returns and reenters the process again. Cases with and without reaction will be discussed. Purge and bypass will also be explained along with the industrial uses of material balances.

12.1 Introduction

In Chapters 9 and 10 we restricted the discussion and examples to a single unit with stream inputs and outputs as illustrated in Figure 12.1a. In Chapter 11 you encountered multiple units but the stream flows still were all in a forward direction representing serial sequences as in Figure 12.1b. In this chapter we take up processes in which material is **recycled**, that is fed back from a downstream unit to an upstream unit, as shown in Figure 12.1c. The stream containing the recycled material is known as a **recycle stream**.

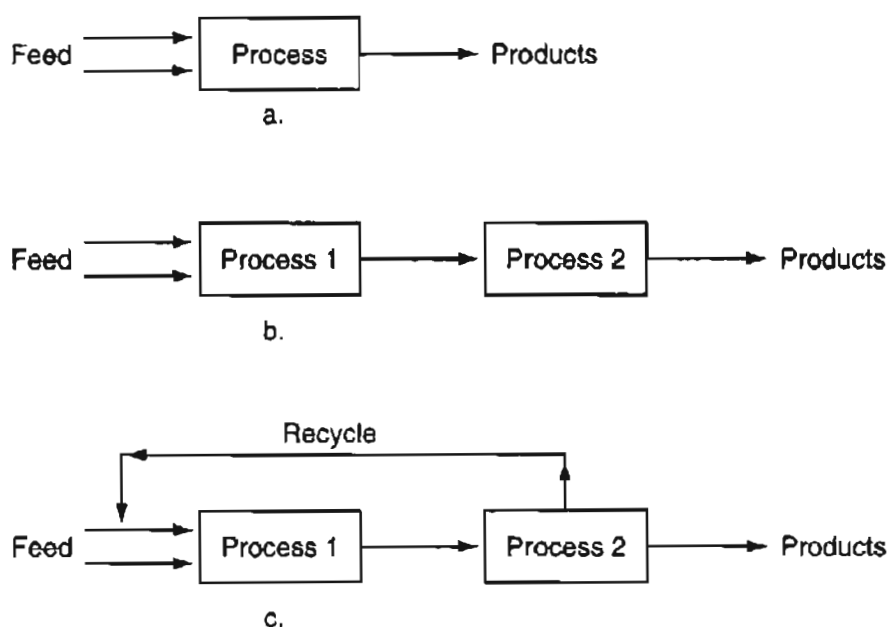


Figure 12.1 Figure 12.1a shows a single unit with serial flows. Figure 12.b shows multiple units but still with serial flows. Figure 12.1c shows the addition of recycle.

What is a **recycle system**? A recycle system is a system that includes one or more recycle streams.

You can see in Figure 12.1c that the recycle stream is mixed with the feed stream, and the combination fed to Process 1. The products from Process 1 are separated in Process 2 into (a) the products and (b) the recycle stream. The recycle stream is returned to Process 1 for further processing. Figure 12.2 illustrates a more complex process involving several recycle streams.

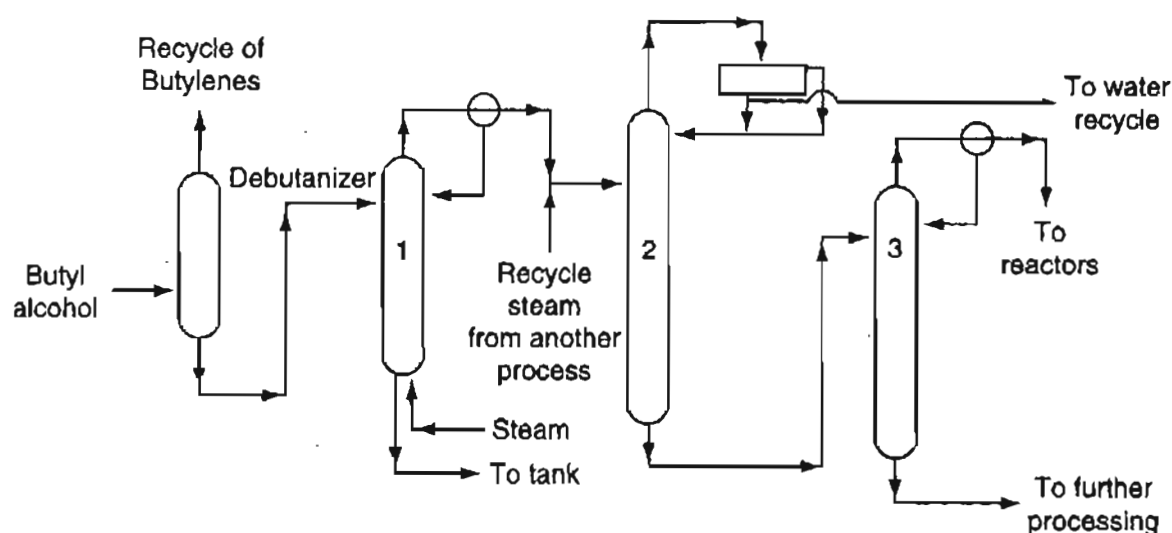


Figure 12.2 A process involving multiple recycle streams comprised of a debutanizer and three distillation columns. Recycle streams from adjacent processes are feeds to this process, and some of the products of this process become recycle streams fed to other processes.

Recycle systems can be found in everyday life. Used newspaper is collected from households, processed to remove the ink, and used to print new newspapers. Clearly, the more newspapers recycled, the fewer trees that have to be consumed to produce newspapers. Recycling of glass, aluminum cans, plastics, copper, and iron are also common.

Recycle systems also occur in nature. For example, consider the “water cycle” shown in Figure 12.3. If a section of the earth is the system, the recycle stream consists of evaporated water that falls to earth as precipitation, and the flow of water in creeks and rivers brings the water back into the system.

Because of the relatively high cost of industrial feedstocks, when chemical reactions are involved in a process, recycle of unused reactants to the reactor can offer significant economic savings for high-volume processing systems. Heat recovery within a processing unit (energy recycle) reduces the overall energy consumption of the process. **Process integration** is terminology applied to using material and energy recycle in process design.

Here are some examples of the application of material recycling in the process industries.

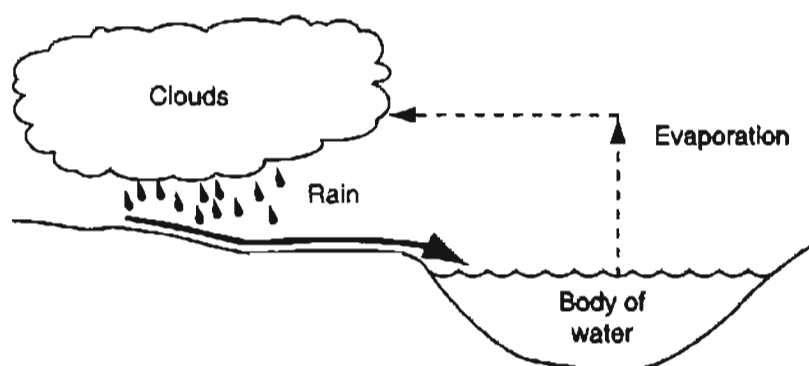


Figure 12.3 A portion of the water cycle.

- 1. Increased reactant conversion.** Recycling the reactants back to the feed to a reactor can significantly increase the overall conversion of the reactants. For certain systems recycle allows the reactor to be operated at low conversion levels, yielding improved selectivity, with recycling of the unreacted reactants making it possible to attain a high overall degree of conversion.
- 2. Continuous catalyst regeneration.** Catalysts are used to increase the rate of chemical reactions, but their effectiveness can diminish with use (catalyst deactivation). Processes that use catalysts that deactivate at a relatively fast rate may require the onsite regeneration and recycling of the catalyst. For example, in a fluidized catalytic cracking (FCC) process (Figure 12.4), the cracking catalyst deactivates almost immediately upon contact with the gas oil feed at the reaction temperature because of the formation of coke on the surface of the catalyst. Therefore, the deactivated (spent) catalyst is transported to the catalyst regenerator where most of the coke is burned off the surface of the catalyst to restore the activity of the catalyst.

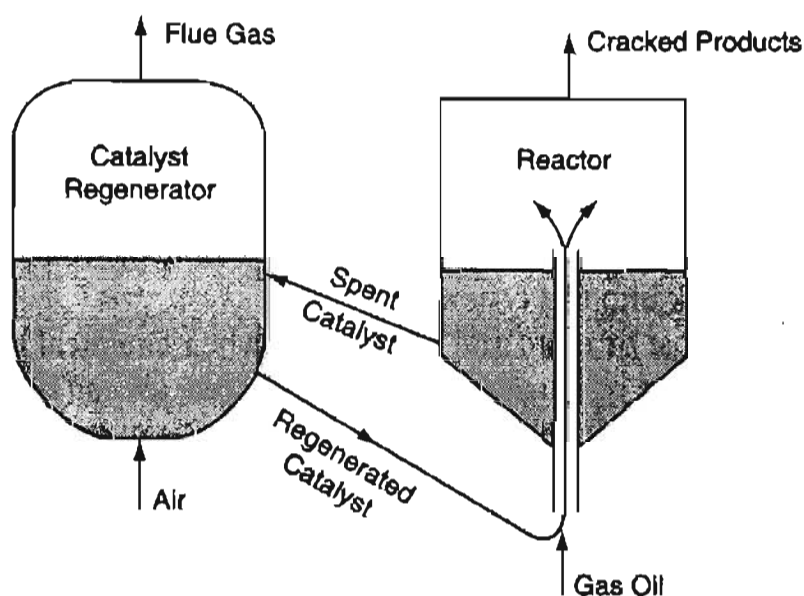


Figure 12.4 Diagram of a FCC process.

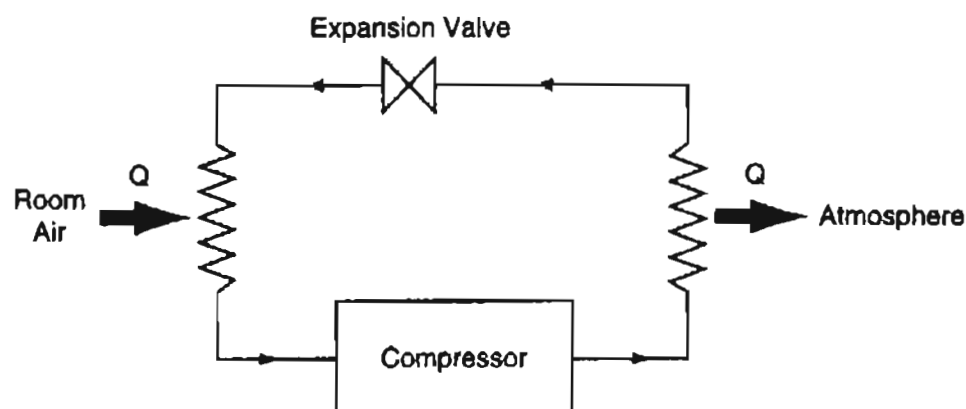


Figure 12.5 Schematic for a closed refrigeration cycle.

3. **Circulation of a working fluid.** A number of processes use the closed circulation of a working fluid for heating or refrigeration. Refrigeration systems (Figure 12.5), including home air conditioning systems, circulate a refrigerant gas by a compressor so that the gas absorbs heat from the room air and discharges heat to the outside atmosphere.

Frequently Asked Questions

If you feed material to a stream continuously, as in Figure 12.1c, why does the amount of the material in the recycle stream not increase and continue to build up?

What is done in this and subsequent chapters is to assume, often without so stating, that the entire process including all units and all of the flows of material are *in the steady state*. As the process starts up or shuts down, the flows in many of the streams change, but once the steady state is reached, “what goes in must come out” applies to the recycle stream as well as the other streams in the process.

You will find that systems involving recycle streams can be quantitatively analyzed without applying any new principles. The procedures developed in Chapters 9, 10, and 11 can be directly applied to systems with recycle.

SELF-ASSESSMENT TEST

Questions

1. Explain the purpose of using recycle in a process.
2. Will a recycle stream always have the same composition as a product stream?

Problems

1. How many recycle streams occur in Figure SAT12.1P1?

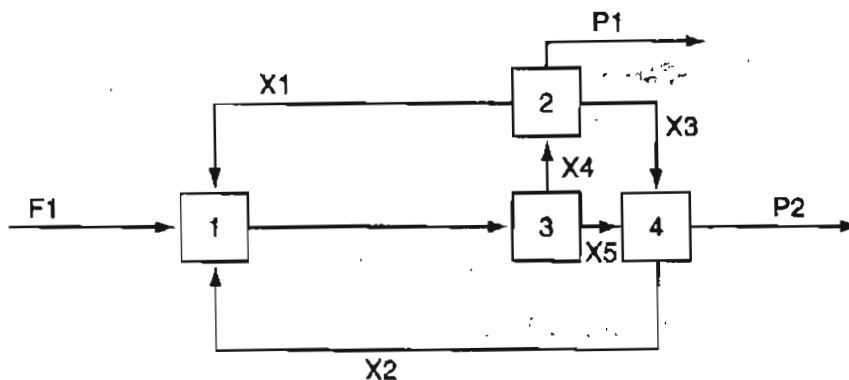


Figure SAT12.1P1

2. The Hooker Chemical Corporation operates a process in Michigan for the purification of HCl. Figure SAT12.1P2 shows the flow sheet for the Hooker process. The streams from the bottoms of the five towers are liquid. The streams from the tops of the towers are gases. HCl is insoluble in the HCB (hexachlorobutadiene). The various stream compositions are shown in Figure SAT12.1P2.

How many recycle streams are there in the Hooker process?

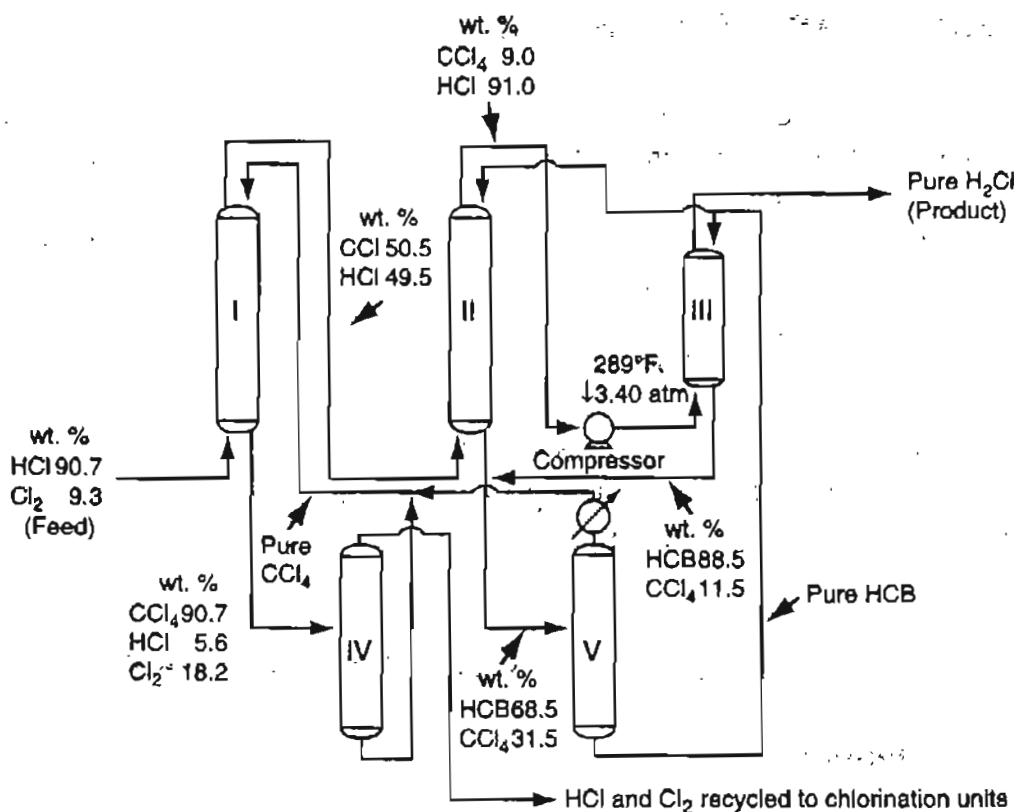


Figure SAT12.1P2

12.2 Recycle without Chemical Reaction

Recycle of material occurs in a variety of processes that do not involve chemical reaction, including distillation, crystallization, and heating and refrigeration systems. As an example of a recycle system, look at the process of drying lumber shown in Figure 12.6. If dry air is used to dry the wood, the lumber will warp and crack. By recycling the moist air that exits from the drier and mixing it with dry air, the inlet air can be maintained at a safe water content to prevent warping and cracking of the lumber.

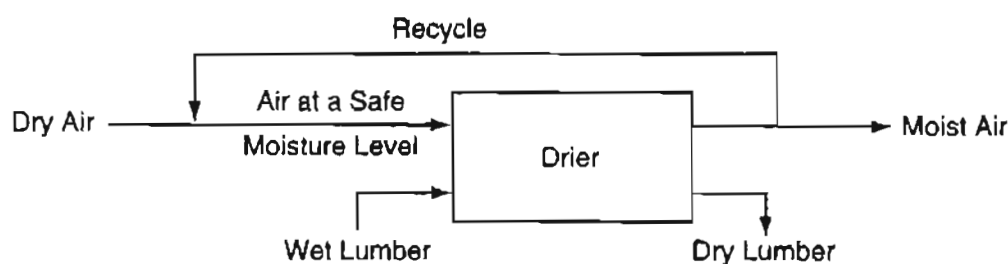


Figure 12.6 Lumber drying process.

Another example, shown in Figure 12.7, is a distillation column used to separate two compounds. Note that a portion of the exit flow from the accumulator is recycled back into the column as **reflux** while the reboiler vaporizes part of the liquid in the bottom of the column to create the vapor flow up the column. The recycle of vapor from the reboiler and return of the liquid from the accumulator back into the column maintain good vapor and liquid contact on the trays inside the column. The contact aids in concentrating the more volatile components in the overhead vapor stream and concentrating the less volatile components in the liquid collected in the bottom of the column.

You can formulate material balances for recycle systems without reaction exactly as you formulated material balances for processes without recycle, as explained in Chapter 7 and subsequent chapters.

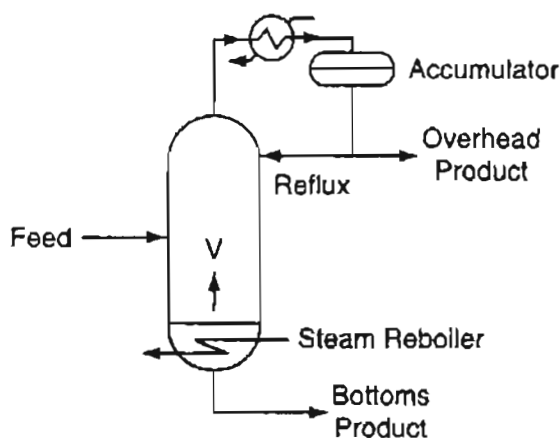


Figure 12.7 Schematic of a two-product distillation column.

The first step in problem solving is to pick a good system(s) for analysis. Examine Figure 12.8. You can write material balances for several different systems, four of which are shown by dashed lines in Figure 12.8, namely:

1. About the entire process including the recycle stream, as indicated by the dashed lines identified by 1 in Figure 12.8. These balances contain no information about the recycle stream. Note that the **fresh feed** enters the overall system and the **overall or net product** is removed.
2. About the junction point (mixing point) at which the fresh feed is combined with the **recycle stream** (identified by 2 in Figure 12.8) to produce the **total, or gross, feed**. These balances do contain information about the recycle stream.
3. About the basic process itself (identified by 3 in Figure 12.8). These balances do not contain any information about the recycle stream. Note that the **total (gross) feed** enters the process and the **gross product** is removed.
4. About the junction point at which the gross product is separated into recycle and overall (net) product (identified by 4 in Figure 12.8). These balances do contain information about the recycle stream.

In addition, you can make balances (not shown in Figure 12.8) about combinations of subsystems, such as the process plus the separator (3 plus 4), or the mixing point plus the process (2 plus 3). These balances added to the set of balances for the individual units would not be independent balances, but might be convenient to use, and serve as substitutes for some of the unit balances.

Note that in Figure 12.8 the recycle stream is associated both with the mixer, which is located at the beginning of the process, and with the separator, which is located at the end of the process. As a result, recycle problems lead to coupled equations that must be solved simultaneously. Therefore, sets of equations involving recycle typically require robust computer software to avoid trouble in solving the equations. You will find that overall material balances (1 in Figure 12.8), particu-

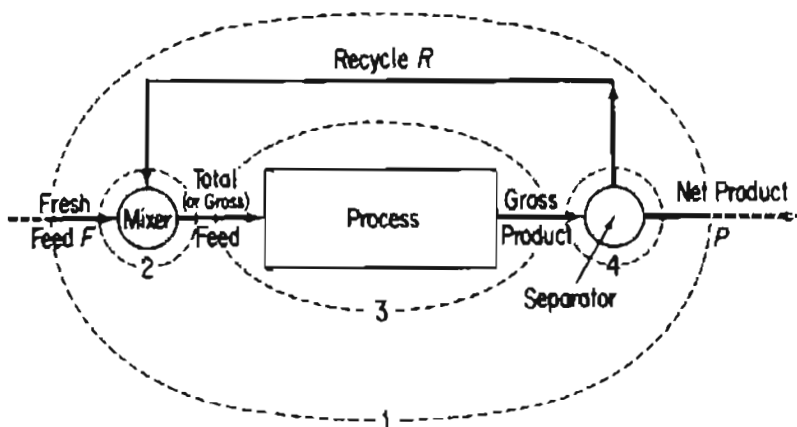


Figure 12.8 Process with recycle (the numbers designate possible system boundaries for the material balances; see the text).

larly involving a tie component, are usually a good place to start when solving recycle problems. If you solve an overall material balance(s), and calculate all or some of the unknowns, the rest of the problem can usually be solved by sequentially applying single unit material balances through the process. If you start solving a recycle problem by writing material balances for individual units, and skip the overall balances, you will probably write an excessive number of equations that have to be solved simultaneously.

EXAMPLE 12.1 A Continuous Crystallizer Involving a Recycle Stream

Figure E12.1a is a schematic of a process for the production of flake NaOH, which is used in households to clear plugged drains in the plumbing (e.g., Drano).

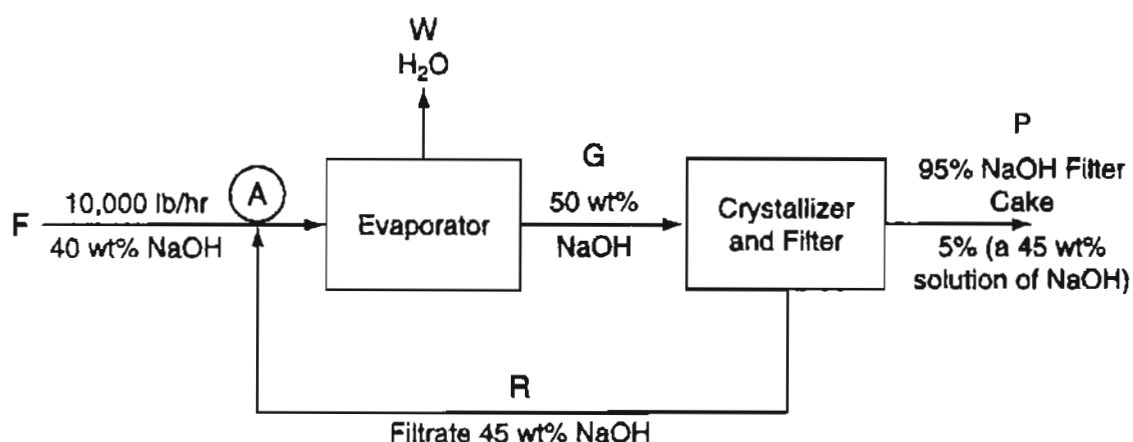


Figure E12.1a

The fresh feed to the process is 10,000 lb/hr of a 40% aqueous NaOH solution. The fresh feed is combined with the recycled filtrate from the crystallizer, and fed to the evaporator where water is removed to produce a 50% NaOH solution, which in turn is fed to the crystallizer. The crystallizer produces a filter cake that is 95% NaOH crystals and 5% solution that itself consists of 45% NaOH. The filtrate contains 45% NaOH.

- You are asked to determine the flow rate of water removed by the evaporator, and the recycle rate for this process.
- Assume that the same production rate of NaOH flakes occurs, but the filtrate is not recycled. What would be the total feed rate of 40% NaOH have to be then? Assume that the product solution from the evaporator still contains 50% NaOH.

Solution

Open, steady-state process

a. Steps 1, 2, 3, and 4

Figure E12.1a contains the information needed to solve the problem.

Step 5

Basis: 10,000 lb fresh feed (equivalent to 1 hour)

Steps 6 and 7

The unknowns are W , G , P , and R . You can make two component balances about three systems: the mixing point A, the evaporator, and the crystallizer as well as two overall component balances. You can also make total balances for the same selection of systems. What balances should you choose to solve the problem? If you plan to put four equations in an equation solver, it does not make any difference as long as the equations are independent. But if you solve the problem by hand, you should count the number of unknown variables involved for each of the three sub-systems and the overall system as follows:

<i>Component balances</i>	<i>Unknowns</i>
Mixing point	R plus feed (and compositions) to evaporator (not labeled)
Evaporator	W , G , and feed to evaporator
Crystallizer	G , P , and R
Overall	W and P

You can see that by using just two overall component balances (you can substitute the overall total balance for one component balance) you can determine the values of W and P . Consequently, you should start with overall balances.

Steps 8 and 9

Overall NaOH balance

$$(0.4)(10,000) = [0.95 + (0.45)(0.05)]P$$

$$P = 4113 \text{ lb}$$

Overall H₂O balance

$$(0.6)(10,000) = W + [(0.55)(0.05)](4113)$$

$$W = 5887 \text{ lb}$$

(or use the overall total balance $10,000 = 4113 + W$)

The total amount of NaOH exiting with P is

$$[(0.95) + (0.45)(0.05)](4113) = 4000 \text{ lb}$$

Are you surprised at this result? You shouldn't be. If you put 4000 lb of NaOH into the process, 4000 lb should come out. The amount of water in P is 113 lb. As a check, $113 + 5887 = 6000$ lb as expected.

Steps 6 and 7 (repeated)

Now that you know W and P , the next step is to make balances on a system that involves the stream R . Choose either the mixing point A or the crystallizer. Which one should you pick? The crystallizer involves three unknowns, and you now know the value of P , so that only two unknowns are involved versus introducing a considerable number of new unknowns if you chose mixing point A as the system.

Steps 8 and 9 (repeated)

NaOH balance on the crystallizer

$$0.5G = 4000 + 0.45R$$

H₂O balance on the crystallizer

$$0.5G = 113 + 0.55R$$

(or use the total balance $G = R + 4113$)

$$R = 38,870 \text{ lb}$$

- b. Now, suppose recycle from the crystallizer does not occur, but the production and composition of P remains the same. Then the output of the crystallizer is just P , as indicated in Figure E12.1b. How should you proceed? Do you recognize that the problem is analogous to the ones that you read about in Chapter 11?

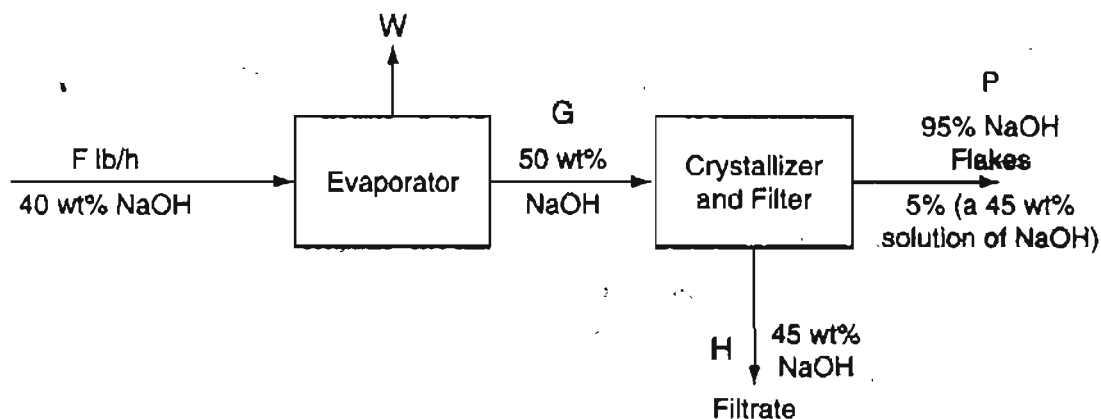


Figure E12.1b

Step 5

The basis is now $P = 4113$ lb (the same as 1 hour)

Steps 6 and 7

The unknowns are now F , W , G , and H . You can make two component balances on the evaporator and two on the crystallizer plus two overall balances. Only four are independent. The evaporator balances would involve F , W , and G . The crystallizer balances would involve G and H while the overall balances would involve F , W , and H . Which balances are best to start with? If you put the equations in an equation solver, it makes no difference which four equations you use as long as they are independent. The crystallizer balances are best to start with by hand because then you have to solve just two pertinent equations for G and H .

Steps 8 and 9

NaOH balance on the crystallizer

$$0.5G = [(0.95) + (0.05)(0.45)](4113) + 0.45H$$

H₂O balance on the crystallizer

$$0.5G = [(0.05)(0.55)](4113) + 0.55H$$
$$H = 38,870 \text{ lb}$$

An overall NaOH balance gives the new F

Overall NaOH balance

$$0.40F = 0.45(38,870) + 4000$$
$$F = 53,730 \text{ lb}$$

Note that without recycle, the feed rate must be 5.37 times larger than with recycle to produce the same amount of product, not to mention the fact that you would have to dispose of a large volume of filtrate.

SELF-ASSESSMENT TEST

Questions

1. Why have we not considered the buildup of material in recycle streams in this chapter?
2. Under what circumstances might material be accumulated or depleted in a recycle stream?
3. Can you make material balances in both steady-state and unsteady-state flow processes that involve recycle?
4. Can you formulate sets of equations that are not independent if recycling occurs in a system?

Problems

1. A ball mill grinds plastic to make a very fine powder. Look at Figure SAT12.2P1.

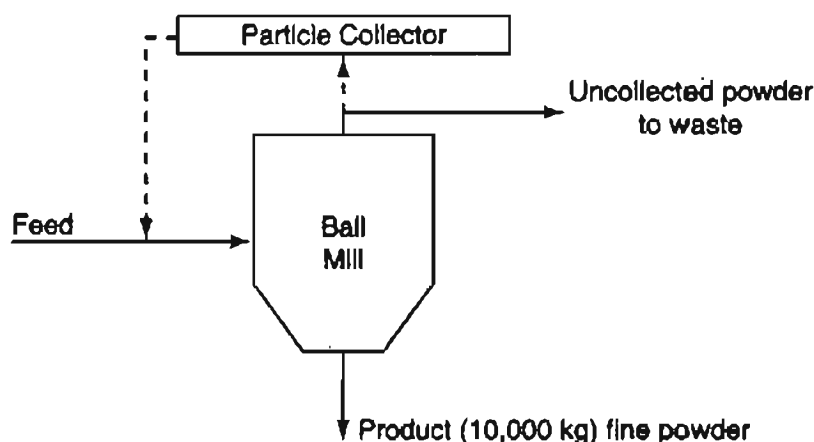


Figure SAT12.2P1

At the present time 10,000 kg of powder are produced per day. You observe that the process (shown by the solid lines) is inefficient because 20% of the feed is not recovered as powder—it goes to waste.

You make a proposal (designated by the dashed lines) to recycle the uncollected material back to the feed so that it can be remilled. You plan to recycle 75% of the 200 kg of uncollected material back to the feed stream. If the feed costs \$1.20/kg, how much money would you save per day while producing 10,000 kg of fine powder?

- Sea water is to be desalinated by reverse osmosis using the scheme indicated in Figure SAT12.2P2. Use the data given in the figure to determine: (a) the rate of waste brine removal (B); (b) the rate of desalinated water (called potable water) production (P); (c) the fraction of the brine leaving the reverse osmosis cell (which acts in essence as a separator) that is recycled.

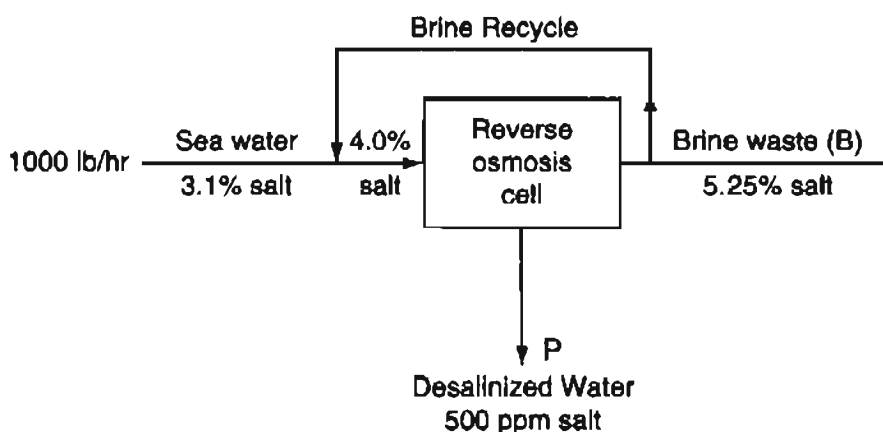


Figure SAT12.2P2

- A material containing 75% water and 25% solid is fed to a granulator at a rate of 4000 kg/hr. The feed is premixed in the granulator with recycled product from a dryer, which follows the granulator (to reduce the water concentration of the overall material fed into

the granulator to 50% water, 50% solid). The product that leaves the dryer is 16.7% water. In the dryer, air is passed over the solid being dried. The air entering the dryer contains 3% water by weight (mass), and the air leaving the dryer contains 6% water by weight (mass).

- What is the ratio of the recycle to the feed entering the granulator?
 - What is the rate of air flow to the dryer on a dry basis?
4. Benzene, toluene, and other aromatic compounds can be recovered by solvent extraction with sulfur dioxide (SO_2). Figure SAT12.2P4 is the process schematic. As an example, a catalytic reformat stream containing 70% benzene and 30% nonbenzene material is passed through the countercurrent extractive recovery scheme shown in Figure SAT12.2P4. 1000 lb of reformat and 3000 lb of SO_2 are fed to the system per hour. The benzene product stream contains 0.15 lb of SO_2 per lb of benzene. The raffinate stream contains all the initially charged nonbenzene material as well as 0.25 lb of benzene per lb of nonbenzene material. The remaining component in the raffinate stream is SO_2 . How many lb of benzene are extracted in the product stream on an hourly basis? How many lb of raffinate are produced per hour?

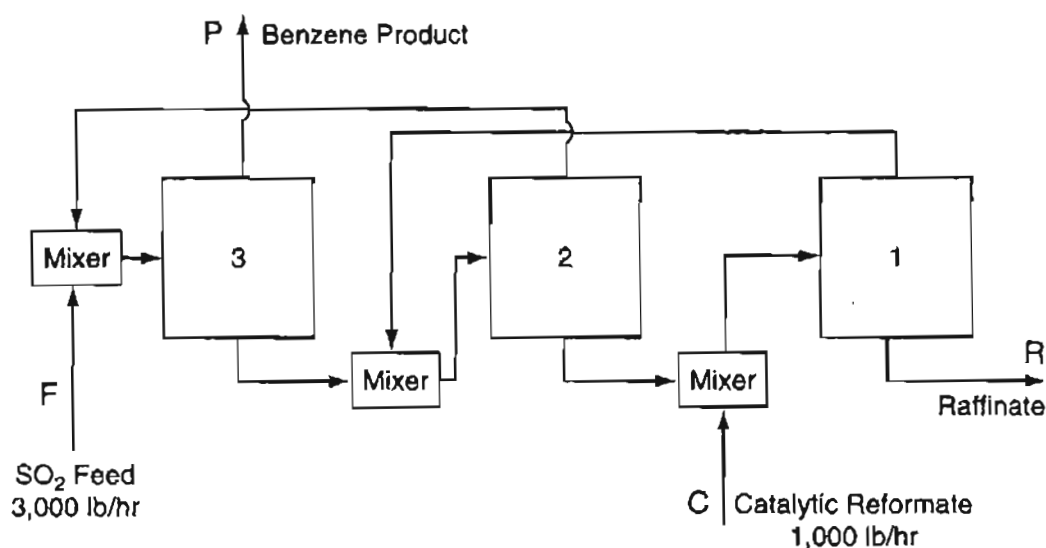


Figure SAT12.2P4

Thought Problem

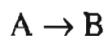
- Centrifugal pumps cannot run dry, and must have a minimum fluid flow to operate properly—to avoid cavitation, and subsequent mechanical damage to the pump. A storage tank is to be set up to provide liquid flow to a process, but sometimes the demand will drop below the minimum flow rate (10–15% of the rated capacity of the pump). What equipment setup would you recommend be implemented so that the pump is not damaged by the low flows? Draw a picture of the layout so that the minimum flow can go through the pump no matter what the level of liquid is in the feed tank and no matter what the outlet pressure and demand may be.

Discussion Problems

1. Because of limitations in supply as well as economics, many industries reuse their water over and over again. For example, recirculation occurs in cooling towers, boilers, powdered coal transport, multistage evaporation, humidifiers, and many devices to wash agricultural products.
Write a brief report discussing one of these processes, and include in the report a description of the process, a simplified flow sheet, problems with recycling, the extent of purge, and, if you can find the information, the savings made by recycling.
2. A series of units with forward and reverse flow, and recycle among units, is known as a cascade. The enrichment of natural uranium by gas diffusion of uranium hexafluoride is a well-known example of a process involving a cascade. Develop a flowsheet of a cascade, and indicate what the material balances are for individual units at the beginning, middle, and end of the cascade.
3. The Celanese company appealed to the Supreme Court the application of an EPA rule concerning benzene leakage to the atmosphere. Four of their plants used benzene in their processes, recycling the benzene over and over in the plants. The company believed that the EPA rule on use applied to the inventory (storage) of benzene, which was far less than the 1000-metric-ton regulatory threshold for "use," whereas the EPA interpretation of the "use" of the benzene was it should be counted each time it circulated through a plant. The EPA argument was that every time the benzene circulated through a plant, it had the same chance of leaking into the air as new benzene would. What is your opinion about this argument? (The U.S. Court of Appeals agreed with the EPA.)

12.3 Recycle with Chemical Reaction

The most common application of recycle for systems involving chemical reaction is the recycle of reactants, an application that is used to increase the overall conversion in a reactor. Figure 12.9 shows a simple example for the reaction



From the data in Figure 12.9 you can see that the steady-state material balances for the mixer, reactor, and separator are satisfied. Also, note that for the overall material balance if you calculate the extent of reaction you will find it is 100 reacting g mol/s.

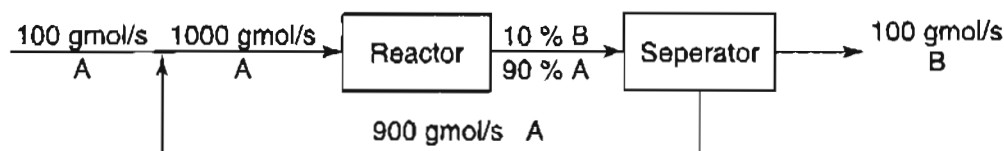


Figure 12.9 A simple recycle system with chemical reaction.

If you calculate the extent of reaction for the overall process in Figure 12.9 based on B

$$\xi_{\text{overall}} = \frac{100 - 0}{1} = 100 \text{ moles reacting}$$

If you use material balances to calculate the output P of the reactor (on the basis of 1 second) you get

$$A = 900 \text{ g mol}$$

$$B = 100 \text{ g mol}$$

and the extent of reaction based on B for the reactor by itself as the system is

$$\xi_{\text{reactor}} = \frac{100 - 0}{1} = 100 \text{ moles reacting}$$

In general, **the extent of reaction is the same regardless of whether an overall material balance is used or a material balance for the reactor is used.** This important fact can be used in solving material balances for recycle systems with reactions.

You will encounter two types of conversion when reactions occur:

1. Overall fraction conversion:

$$\frac{\text{mass (moles) of reactant in the fresh feed} - \text{mass (moles) of reactant in the output of the overall process}}{\text{mass (moles) of reactant in the fresh feed}}$$

2. Single - pass ("once - through") fraction conversion:

$$\frac{\text{mass (moles) of reactant fed into the reactor} - \text{mass (moles) of reactant exiting the reactor}}{\text{mass (moles) of reactant fed into the reactor}}$$

As the name indicates, the overall conversion depends only on what enters and leaves the overall process, while the single-pass conversion depends on what enters and leaves the reactor. For the simple recycle reactor in Figure 12.9, the overall conversion is 100%

$$\frac{100 - 0}{100} \times 100 = 100\%$$

and the single-pass conversion is 10%

$$\frac{1000 - 900}{1000} \times 100 = 10\%$$

When the fresh feed consists of more than one reactant, the conversion can be expressed for a single component, usually the limiting reactant, or the most impor-

tant (expensive) reactant. Remember from Chapter 10 that conversion in a reactor (the single-pass conversion) can be limited by chemical equilibrium and/or chemical kinetics, but the overall conversion is also limited by the efficiency of the separator in separating compounds to be recycled from the compounds that are not recycled.

The overall conversion (f with a subscript OA) and the single-pass conversion (f with a subscript SP) can be expressed in terms of the extent of reaction, ξ , that was discussed in Chapter 10. From the definition of the overall conversion, note that the numerator is equal to the negative of the product of the extent of reaction times of the stoichiometric coefficient of the reactant (A), and the denominator is the moles of fresh feed of the reactant (A):

$$\text{Overall conversion of species A} = f_{\text{OA}} = \frac{-v_A \xi}{n_A^{\text{fresh feed}}} \quad (12.1)$$

For the single-pass conversion, the numerator is the same product as in Equation (12.1) while the denominator is equal to the amount of the reactant fed to the reactor:

$$\text{Single-pass conversion} = f_{\text{SP}} = \frac{-v_A \xi}{n_A^{\text{reactor feed}}} \quad (12.2)$$

If you solve Equations (12.1) and (12.2) for the extent of reaction, equate the extents, and use a balance at the mixing point $n_{\text{LR}}^{\text{reactor feed}} = n_{\text{LR}}^{\text{fresh feed}} + n_{\text{LR}}^{\text{recycle}}$, you can obtain the following relationship between overall and single-pass conversion:

$$\frac{f_{\text{SP}}}{f_{\text{OA}}} = \frac{n_A^{\text{fresh feed}}}{n_A^{\text{fresh feed}} + n_A^{\text{recycle}}} \quad (12.3)$$

If you now apply Equation (12.3) to the simple recycle example in Figure 12.9, what value do you get for the ratio of the single-pass to overall conversion? Do you get 0.1, which agrees with the result stated previously?

EXAMPLE 12.2 Recycle in a Process in Which a Reaction Occurs

Cyclohexane (C_6H_{12}) can be made by the reaction of benzene (Bz) (C_6H_6) with hydrogen according to the following reaction:



For the process shown in Figure E12.2, determine the ratio of the recycle stream to the fresh feed stream if the overall conversion of benzene is 95%, and the single-pass conversion is 20%. Assume that 20% excess hydrogen is used in the fresh feed, and that the composition of the recycle stream is 22.74 mol % benzene and 78.26 mol % hydrogen.

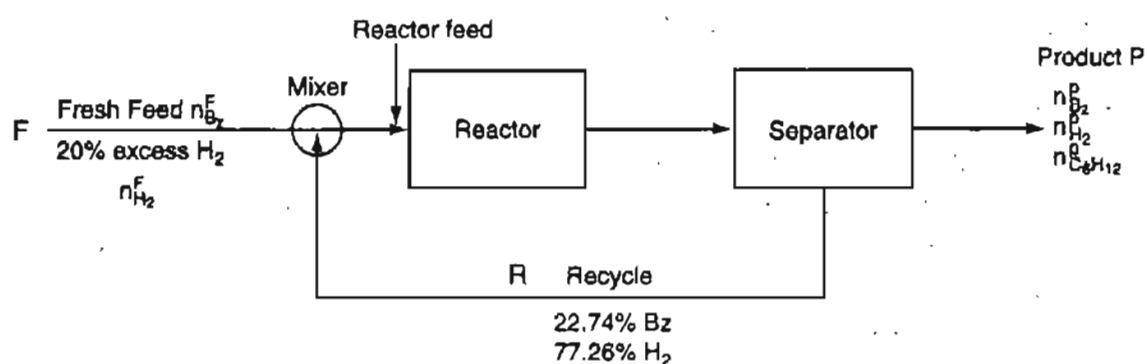


Figure E12.2 Schematic of a recycle reactor.

Also calculate the environmental impact of the product gas by calculating an environmental index based on the following threshold limit values (TLV) for the respective components:

	TLV (ppm)
Benzene	0.5
Cyclohexane	300
Hydrogen	1000

Solution

The process is open and steady state.

Step 5

A convenient basis to choose would be 100 mol (g mol or lb mol) of fresh benzene feed, although you could select the recycle to be 100 mol.

Steps 1, 2, 3, and 4

Figure E12.2 contains all of the information available about the flowstreams except the amount of H_2 , which is in 20% excess (for complete reaction, remember)

$$n_{H_2}^F = 100(3)(1 + 0.20) = 360 \text{ mol}$$

and the total fresh feed is 460 mol.

From Equation (12.1) for benzene ($\nu_{B_z} = -1$)

$$0.95 = \frac{-(-1)\xi}{100}$$

you can calculate that $\xi = 95$ reacting moles.

Steps 6 and 7

The unknowns are R , $n_{B_z}^P$, $n_{H_2}^P$, and $n_{C_6H_{12}}^P$. You can write three species balances for each of the three systems, the mixing point, the reactor, and the separator

plus overall balances (not all of which are independent, of course). Which systems should you choose to start with? The overall process, because then you can use the value calculated for the extent of reaction.

Steps 8 and 9

The species overall balances are $n_i^{\text{out}} = n_i^{\text{in}} + \nu_i \xi_{\text{overall}}$

$$\text{Bz: } n_{\text{Bz}}^{\text{P}} = 100 + (-1)(95) = 5 \text{ mol}$$

$$\text{H}_2: n_{\text{H}_2}^{\text{P}} = 360 + (-3)(95) = 75 \text{ mol}$$

$$\text{C}_6\text{H}_{12}: n_{\text{C}_6\text{H}_{12}}^{\text{P}} = 0 + (1)(95) = \underline{95 \text{ mol}}$$

$$P = 175 \text{ mol}$$

The next step is to use the final piece of information, the information about the single-pass conversion and Equation (12.2), to get R . The system is now the reactor. The amount of the Bz feed to the reactor is $100 + 0.2274R$, and $\xi = 95$ (the same as calculated from the overall conversion). Thus, for benzene

$$0.20 = \frac{-(-1)95}{100 + 0.2274R}$$

and

$$R = 1649 \text{ mol}$$

Finally, the ratio of recycle to fresh feed is

$$\frac{R}{F} = \frac{1649 \text{ mol}}{460 \text{ mol}} = 3.58$$

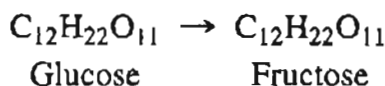
The higher the TLV, the more exposure that can be tolerated, hence an index should use the inverse of the TLV values appropriately weighed. You can use relative concentrations or mole fractions as weights.

$$\text{Environmental index} = \frac{5}{175} \left(\frac{1}{0.5} \right) + \frac{95}{175} \left(\frac{1}{300} \right) + \frac{75}{175} \left(\frac{1}{1000} \right) = 0.059$$

Note that the benzene contributes 96% of the index.

EXAMPLE 12.3 Recycle in a Process with a Reaction Occurring

Immobilized glucose isomerase is used as a catalyst in producing fructose from glucose in a fixed-bed reactor (water is the solvent). For the system shown in Figure E12.3a, what percent conversion of glucose results on one pass through the reactor when the ratio of the exit stream to the recycle stream in mass units is equal to 8.33? The reaction is



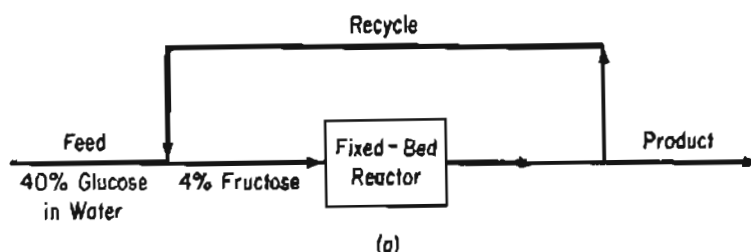


Figure E12.3a

Solution

The process is an open, steady-state process with a reaction occurring and a recycle.

Steps 1, 2, 3, and 4

Figure E12.3b includes all the known and unknown values of the variables using appropriate notation (W stands for water, G for glucose, and F for fructose). Note that the recycle stream and product stream have the same composition, and consequently the same mass symbols are used in the diagram for each stream.

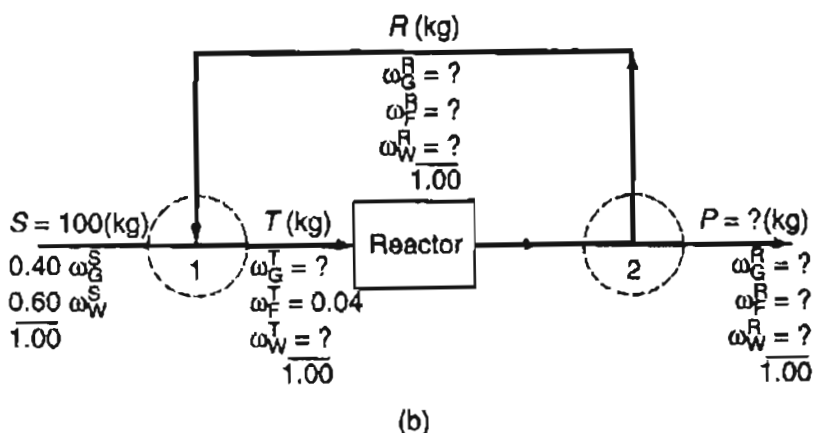


Figure E12.3b

Step 5

Pick as a basis $S = 100$ kg, given the data shown in Figure E12.3b.

Step 6

We have not provided any notation for the reactor exit stream and composition because we will not be using these values in our balances. Let f be the fraction conversion for one pass through the reactor. The unknowns are R , P , T , ω_G^R , ω_F^R , ω_W^R , ω_G^T , ω_F^T , and f , for a total of 9.

Step 7

The balances are $\sum \omega_i^R = 1$, $\sum \omega_i^T = 1$, $R = P/8.33$, plus 3 species balances each on the mixing point 1, the separator 2, and the reactor as well as overall balances.

We will assume we can find 9 independent balances among the lot and proceed. We do not have to solve all of the equations simultaneously. The units are mass (kg).

Steps 8 and 9

We will start with overall balances as they are easy to form and are often decoupled for solution.

Overall balances

$$\text{Total: } P = S = 100 \text{ kg (How simple!)}$$

$$\text{Consequently, } R = \frac{100}{8.33} = 12.0 \text{ kg}$$

Overall no water is generated or consumed, hence

$$\begin{aligned} \text{Water: } 100(0.60) &= P\omega_W^R = 100\omega_W^R \\ \omega_W^R &= 0.60 \end{aligned}$$

We now have 6 unknowns left for which to solve. We start somewhat arbitrarily with mixing point 1 to calculate some of the unknowns

Mixing point 1

No reaction occurs so that species balances can be used without involving the extent of reaction:

$$\text{Total: } 100 + 12 = T = 112$$

$$\text{Glucose: } 100(0.40) + 12\omega_G^R = 112\omega_G^T$$

$$\text{Fructose: } 0 + 12\omega_F^R = 112(0.04)$$

or

$$\omega_F^R = 0.373$$

$$\text{Also, because } \omega_F^R + \omega_G^R + \omega_W^R = 1,$$

$$\omega_G^R = 1 - 0.373 - 0.600 = 0.027$$

Next, from the glucose balance

$$\omega_G^T = 0.360$$

Next, rather than make separate balances on the reactor and separator, we will combine the two into one system (and thus avoid having to calculate values associated with the reactor exit stream).

Reactor plus Separator 2

Total: $T = 12 + 100 = 112$ (a redundant equation)

$$\begin{aligned} \text{Glucose: } \omega_G^T T - (R + P)(\omega_G^R) &= (f)(\omega_G^T T) \\ (0.360)(112) - (112)(0.027) &= f(0.360)(112) \\ 40.3 - 3.02 &= f(40.32) \\ f &= 0.93 \end{aligned}$$

Step 10

Check by using Equation (12.2) and the extent of reaction

$$\xi = \frac{3.02 - 40}{-1} = 37 \quad f = \frac{-(-1)(37)}{40} = 0.93$$

EXAMPLE 12.4 A Bioreactor with Recycle

Reactors that involve biological materials (bioreactors) use living organisms to produce a variety of products. Bioreactors are used for producing ethanol, antibiotics, and proteins for dietary supplements and medical diagnosis. Figure E12.4 shows a recycle bioreactor in which the overall conversion of the proprietary component in the fresh feed to product is 100%. The conversion of the proprietary component to product per pass in the reactor is 40%. Determine the amount of recycle and the mass percent of component in the recycle stream if the product stream contains 90% product, and the feed to the reactor contains 3 wt % of the component.

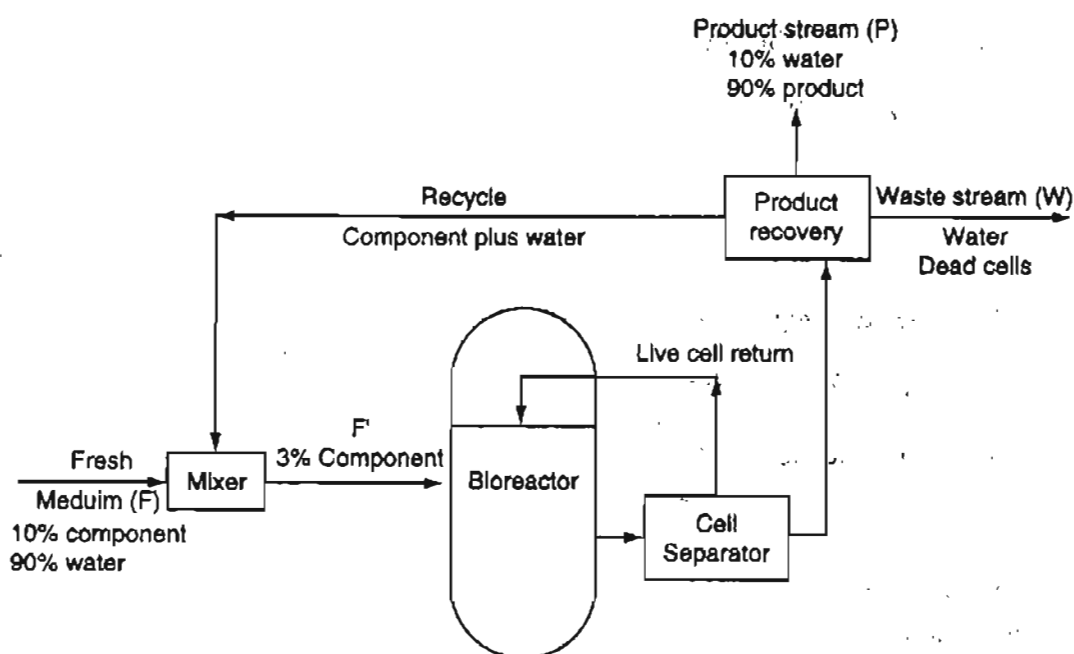


Figure E12.4

Assume that the component and the product have essentially the same molecular weight, and that the waste contains only water and dead cells.

Solution

Steps 2, 3, and 4

All of the data have been inserted in Figure E12.4.

Step 5

Pick a convenient basis of 100 kg of fresh feed (F).

Steps 6 and 7

Pick the *overall process as the system*.

Variables (9): 3 stream flows and 2 compositions in each stream

Equations (9):	Basis	1
	Sum of mass fractions in 3 streams	3
	Specifications: One composition in F (the other is redundant)	1
	One composition in P	1
	Material balances: Component and water (or total)	2
	Percent overall conversion	1
	Total	9

The degrees of freedom are zero.

Steps 8 and 9

Total balance: $100 = P + W$

Component balance: $0.10 (100) = 0.90 P$

$$P = 11.1 \text{ kg} \qquad W = 88.9 \text{ kg}$$

Next pick the *reactor plus the product recovery unit as the system*.

Steps 6 and 7

The degree-of-freedom analysis can be omitted because all that is needed to get the kg of proprietary component in the recycle stream is a component balance using the given 40% single-pass conversion. Let R be the kg of recycle and ω be the mass fraction of component in the recycle stream.

Steps 8 and 9

Apply Equation (10.1) using as units kg (the molecular weight of the component can be eliminated from each term by division). The consumption term represents conversion of 40% of the input term.

Accumulation	Input	Output	Generation	Consumption
0	$= [100 (0.10) + R\omega]$	$- R\omega$	+	0
				$-0.40 [100 (0.10) + R\omega]$

$R\omega = 15 \text{ kg of component in the recycle stream}$

Next, pick the mixer as the system.

Component balance: $100 (0.10) + 15 = 0.03 F'$

Total balance: $R = 833 - 100$

$$\omega = \frac{15}{733} = 0.0205$$

SELF-ASSESSMENT TEST

Questions

1. If the components in the feed to a process appear in stoichiometric quantities and the subsequent separation process is complete so that all of the unreacted reactants are recycled, what is the ratio for reactants in the recycle stream?
2. Answer the following questions true or false:
 - a. The general material balance applies for processes that involve recycle with reaction as it does for other processes.
 - b. The key extra piece of information in material balances on processes with recycle in which a reaction takes place is the specification of the fraction conversion or extent of reaction.
 - c. The degrees of freedom for a process with recycle that involves chemical reaction are the same as for a process without recycle.
3. Cite two reasons for using recycle in a process.

Problems

1. A catalytic dehydrogenation process shown in Figure SAT12.3P1, produces 1, 3 butadiene (C_4H_6) from pure normal butane (C_4H_{10}). The product stream contains 75 mol/hr of H_2 and 13 mol/hr of C_4H_{10} as well as C_4H_6 . The recycle stream is 30% (mol) C_4H_{10} and 70% (mol) C_4H_6 , and the flow is 24 mol/hr.

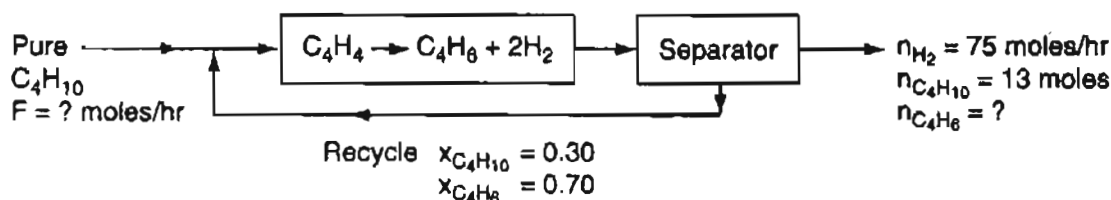


Figure SAT12.3P1

- (a) What is the feed rate, F , and the product flow rate of C_4H_6 leaving the process?
 (b) What is the single-pass conversion of butane in the process?
2. Pure propane (C_3H_8) from El Paso is dehydrogenated catalytically in a continuous process to obtain propylene (C_3H_6). All of the hydrogen formed is separated from the reactor exit gas with no loss of hydrocarbon. The hydrocarbon mixture is then fractionated to give a product stream containing 88 mole % propylene and 12 mole % propane. The other stream, which is 70 mole % propane and 30 mole % propylene, is recycled. The one-pass conversion in the reactor is 25%, and 1000 kg of fresh propane are fed per hour. Find (a) the kg of product stream per hour, and (b) the kg of recycle stream per hour.
3. Ethyl ether is made by the dehydration of ethyl alcohol in the presence of sulfuric acid at 140°C :



Figure SAT12.3P3 is a simplified process diagram. If 87% conversion of the alcohol fed to the reactor occurs per pass in the reactor, calculate: (a) kilograms per hour of fresh feed, and (b) kilograms per hour of recycle.

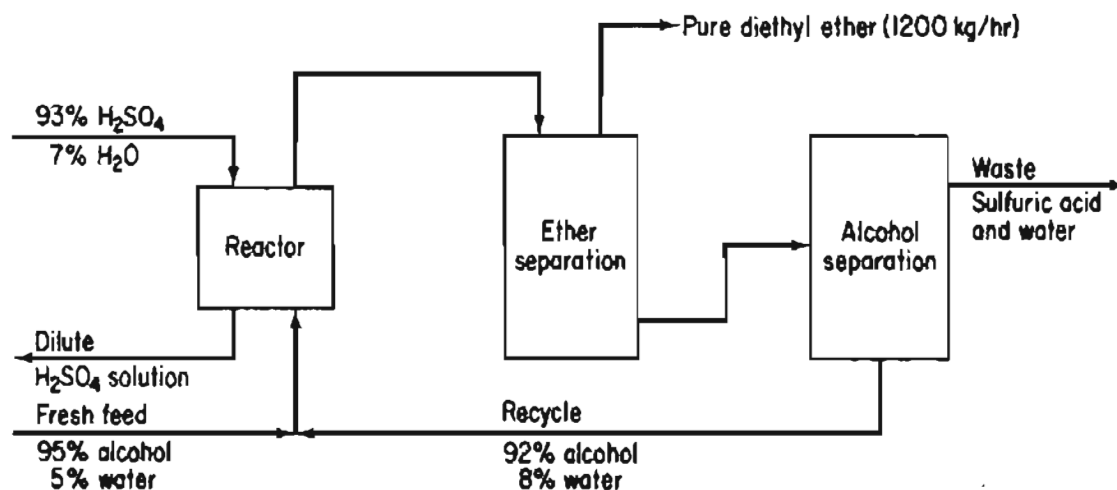


Figure SAT12.3P3

Discussion Problem

1. Numerous techniques have been proposed for desulfurization of flue gases. The techniques can be categorized by the phase in which the reactions occur: gas or solution. What are some of the factors that influence the choice of the process for flue gas desulfurization?

12.4 Bypass and Purge

Two additional commonly encountered types of process streams are shown in Figures 12.10 and 12.11.

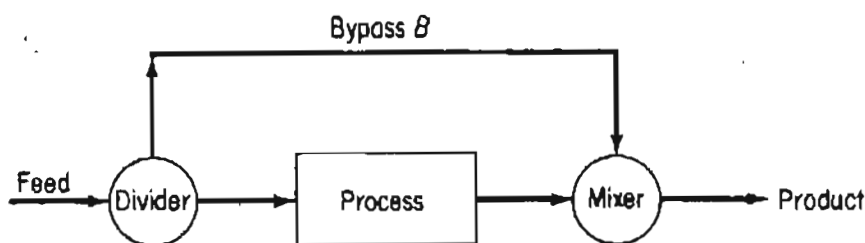


Figure 12.10 A process with a bypass stream.

- a. A **bypass** stream—a stream that skips one or more stages of the process and goes directly to another downstream stage (Figure 12.10).
A bypass stream can be used to control the composition of a final exit stream from a unit by mixing the bypass stream and the unit exit stream in suitable proportions to obtain the desired final composition.
- b. A **purge** stream—a stream bled off from the process to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream (Figure 12.11).

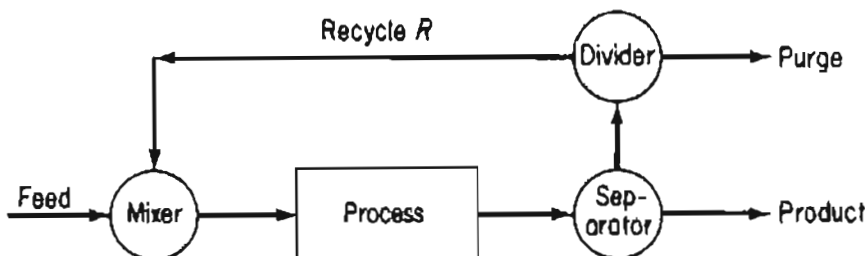


Figure 12.11 A process with a recycle stream with purge.

Many companies have had the unfortunate experience that on startup of a new process, trace components not considered in the material balances used in the design of the process (because the amounts were so small) build up in one or more recycle loops.

Look at Figure 12.12 for an example of a process involving recycle with a purge stream.

Note how in the steady state the argon concentration is different in each successive recycle stream so that 1% argon occurs in the feed stream while 25% argon occurs in the third recycle and purge stream. For effective operation, the Ar concentration cannot be allowed to increase further. Remember that the process operates continuously in the steady state so that the Ar concentration is constant in each individual recycle stream.

Calculations for processes involving bypass and purge streams introduce no new principles or techniques beyond those presented so far. Two examples will make that clear.

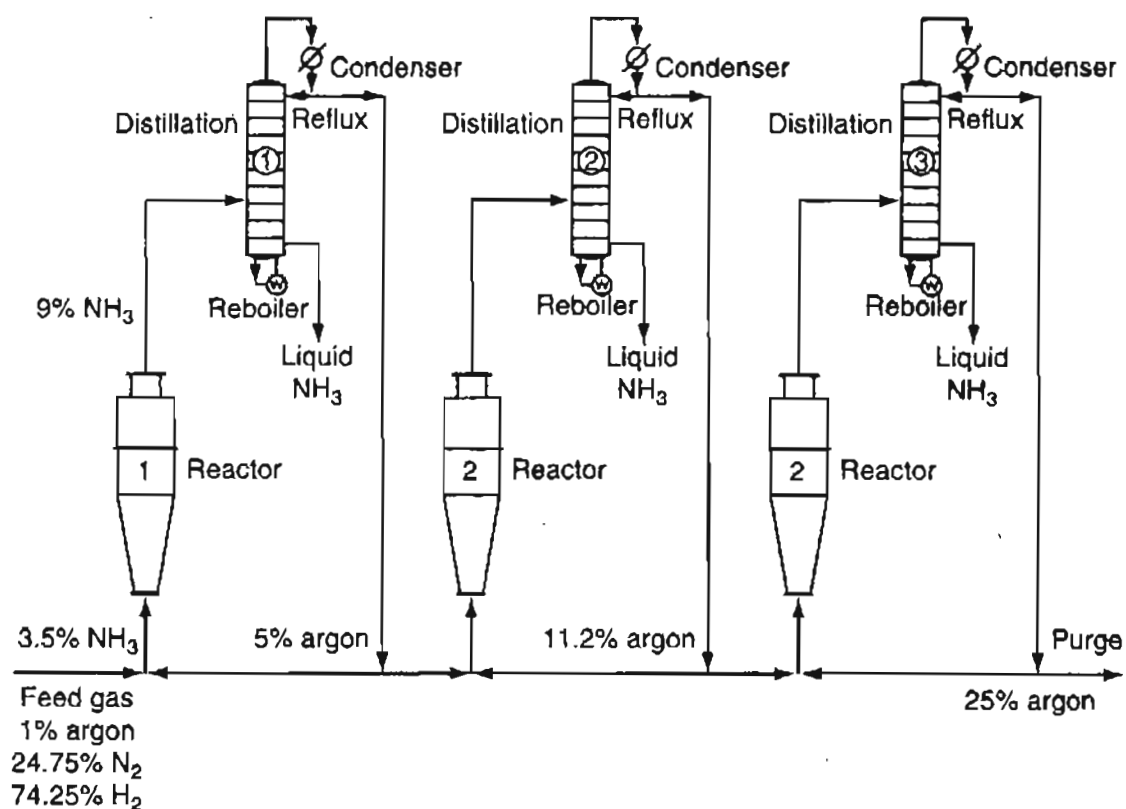


Figure 12.12 A process to manufacture ammonia that involves three reactors and three distillation columns. Note the stepwise rise in the concentration of Ar in the recycle streams.

EXAMPLE 12.5 Bypass Calculations

In the feedstock preparation section of a plant manufacturing natural gasoline, isopentane is removed from butane-free gasoline. Assume for purposes of simplification that the process and components are as shown in Figure E12.5. What fraction

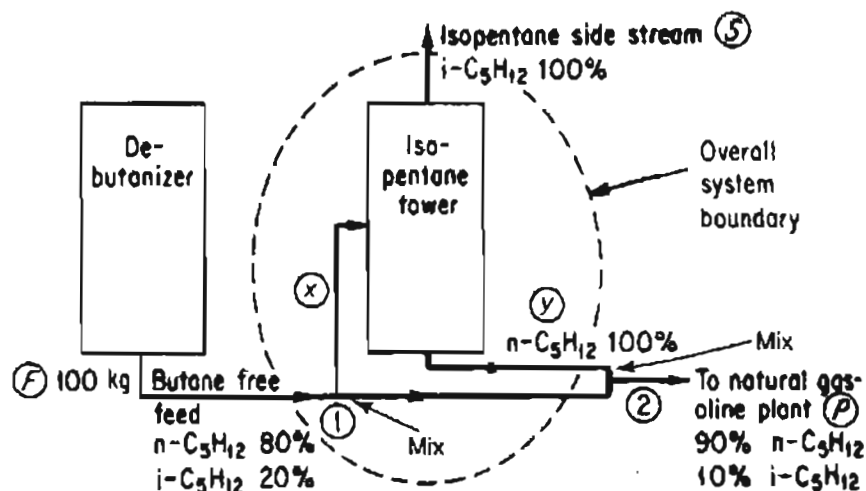


Figure E12.5

of the butane-free gasoline is passed through the isopentane tower? Detailed steps will not be listed in the analysis and solution of this problem. The process is in the steady state and no reaction occurs.

Solution

By examining the flow diagram you can see that part of the butane-free gasoline bypasses the isopentane tower and proceeds to the next stage in the natural gasoline plant. All the compositions (the streams are liquid) are known. Select a basis: 100 kg feed

What kind of balances can you write for this process? You can write the following:

- a. *Overall balances* (each stream is designated by the letter F , S , or P with the units being kg)

Total material balance:

$$\frac{In}{100} = \frac{Out}{S + P} \quad (a)$$

Component balance for $n\text{-C}_5$ (tie component)

$$\frac{In}{100(0.80)} = \frac{Out}{S(0) + P(0.90)} \quad (b)$$

Consequently,

$$P = 100 \left(\frac{0.80}{0.90} \right) = 88.9 \text{ kg}$$

$$S = 100 - 88.9 = 11.1 \text{ kg}$$

The overall balances will not tell you the fraction of the feed going to the isopentane tower. For this calculation you need another balance.

- b. *Balance around isopentane tower:* Let x be the kg of butane-free gas going to the isopentane tower, and y be the kg of the $n\text{-C}_5\text{H}_{12}$ stream leaving the isopentane tower.

Total material balance:

$$\frac{In}{x} = \frac{Out}{11.1 + y} \quad (c)$$

Component balance for $n\text{-C}_5$ (a tie component):

$$x(0.80) = y \quad (d)$$

Consequently, combining (c) and (d) yields

$$x = 55.5 \text{ kg, or the desired fraction is } 0.55.$$

Another approach to this problem is to make a balance at mixing points 1 and 2. Although there are no pieces of equipment at those points, you can see that streams enter and leave the junctions.

c. Balance around mixing point 2:

material into junction = material out

$$\text{Total material: } (100 - x) + y = 88.9 \quad (e)$$

$$\text{Component (iso-C}_5\text{): } (100 - x)(0.20) + 0 = 88.9(0.10) \quad (f)$$

Equation (f) avoids the use of y . Solving yields

$$x = 55.5 \text{ kg as before}$$

EXAMPLE 12.6 Purge

Considerable interest exists in the conversion of coal into more convenient liquid products for subsequent production of chemicals. Two of the main gases that can be generated under suitable conditions from insitu (in the ground) coal combustion in the presence of steam (as occurs naturally in the presence of groundwater) are H_2 and CO . After cleanup, these two gases can be combined to yield methanol according to the following equation

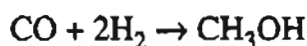


Figure E12.6 illustrates a steady-state process for the production of methanol. All of the compositions are in mole fractions or percent. The stream flows are in moles.

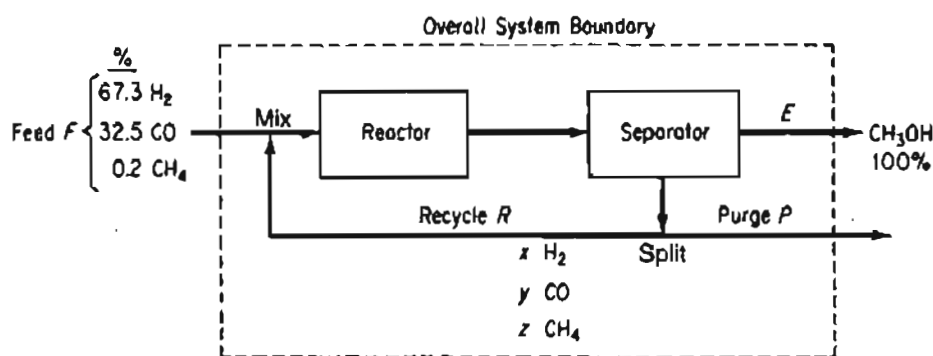


Figure E12.6

Note in Figure E12.6 that some CH_4 enters the process, but does not participate in the reaction. A purge stream is used to maintain the CH_4 concentration in the exit from the separator at no more than 3.2 mol%, and prevent hydrogen buildup as well. The once-through conversion of the CO in the reactor is 18%.

Compute the moles of recycle, CH_3OH , and purge per mole of feed, and also compute the purge gas composition.

Solution**Steps 1, 2, 3, and 4**

All of the known information has been placed on the diagram. The process is in the steady state with reaction. The purge and recycle streams have the same composition (implied by the splitter in the figure). The mole fraction of the components in the purge stream have been designated as x , y , and z for H_2 , CO , and CH_4 , respectively.

Step 5

Select a convenient basis: $F = 100$ mol

Step 6

The variables whose values are unknown are x , y , z , E , P , and R . You can ignore the stream between the reactor and separator as no questions are asked about it.

Step 7

Because the problem is presented in terms of moles, making an overall mass balance is not convenient. Instead we will use element balances. You can make three independent element balances for the overall process: H, C, and O balances. If you make a CO species balance on the reactor plus separator, you can use the information about the percent conversion of CO to provide one additional balance. How can you obtain fifth and sixth balances so that the system of equations is determinate? One piece of information given in the problem statement that has not been used is the information about the upper limit on the CH_4 concentration in purge stream. This limit can be expressed as $z \leq 0.032$. Assume that the purge stream contains the maximum allowed CH_4 so that you can get an equation, thus making

$$z = 0.032 \quad (a)$$

Another piece of information is the implicit mole fraction balance in the recycle stream

$$x + y + z = 1 \quad (b)$$

Steps 8 and 9

The overall element balances are (in moles):

$$2H: 67.3 + 0.2(2) = E(2) + P(x + 2z) \quad (c)$$

$$C: 32.5 + 0.2 = E(1) + P(y + z) \quad (d)$$

$$O: 32.5 = E(1) + P(y) \quad (e)$$

For a system composed of the reactor plus the separator (chosen to avoid calculating the unknown information about the direct output of the reactor), the CO balance is

$$\text{CO: } \frac{\text{In}}{[32.5 + Ry]} - \frac{\text{Out}}{[y(R + P)]} = \frac{\text{Consumed}}{(32.5 + Ry)(0.18)} \quad (\text{f})$$

Equation (a) can be substituted into Equations (b) through (f), and the resulting five equations solved by successive substitution or by using a computer program. The resulting values obtained are (in moles)

<i>E</i>	CH ₃ OH	31.25
<i>P</i>	purge	6.25
<i>R</i>	recycle	705
<i>x</i>	H ₂	0.768
<i>y</i>	CO	0.200
<i>z</i>	CH ₄	0.032

Step 10

Check to see that each of the balances (b)–(f) is satisfied.

If you want to use the extent of reaction to make the calculations, you must first calculate ξ^{\max} for CO and H₂, and then find that CO was the limiting reactant. You could reach the same conclusion by inspection. Then

$$0.18 = \frac{-(-1)\xi}{32.5 + Ry} \quad \text{and} \quad E = 0 + (1)\xi \quad \text{would be equations to use.}$$

SELF-ASSESSMENT TEST

Questions

1. Explain what bypass means in words and also by a diagram.
2. Answer the following questions true or false:
 - a. Purge is used to maintain a concentration of a minor component of a process stream below some set point so that it does not accumulate in the process.
 - b. Bypassing means that a process stream enters the process in advance of the feed to the process.
 - c. A trace component in a stream or produced in a reactor has negligible effect on the overall material balance when recycle occurs.
3. Is the waste stream the same as a purge stream in a process?

Problems

1. In the famous Haber process (Figure SAT12.4P1) to manufacture ammonia, the reaction is carried out at pressures of 800 to 1000 atm and at 500 to 600°C using a suitable catalyst. Only a small fraction of the material entering the reactor reacts on one pass, so recycle is needed. Also, because the nitrogen is obtained from the air, it contains almost 1% rare gases (chiefly argon) that do not react. The rare gases would continue to build up in

the recycle until their effect on the reaction equilibrium would become adverse. Therefore, a small purge stream is used.

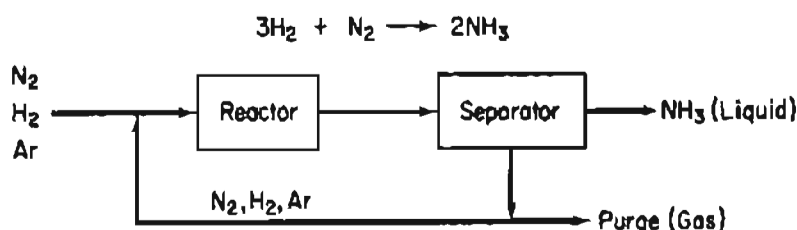


Figure SAT12.4P1

The fresh feed of gas composed of 75.16% H_2 , 24.57% N_2 , and 0.27% Ar is mixed with the recycled gas and enters the reactor with a composition of 79.52% H_2 . The gas stream leaving the ammonia separator contains 80.01% H_2 and no ammonia. The product ammonia contains no dissolved gases. Per 100 moles of fresh feed:

- How many moles are recycled and purged?
 - What is the percent conversion of hydrogen per pass?
2. Figure SAT12.4P2 shows a simplified process to make ethylene dichloride ($\text{C}_2\text{H}_4\text{Cl}_2$). The feed data have been placed on the figure. Ninety percent conversion of the C_2H_4 occurs on each pass through the reactor. The overhead stream from the separator contains 98% of the Cl_2 entering the separator, 92% of the entering C_2H_4 , and 0.1% of the entering $\text{C}_2\text{H}_4\text{Cl}_2$. Five percent of the overhead from the separator is purged. Calculate (a) the flow rate and (b) the composition of the purge stream.

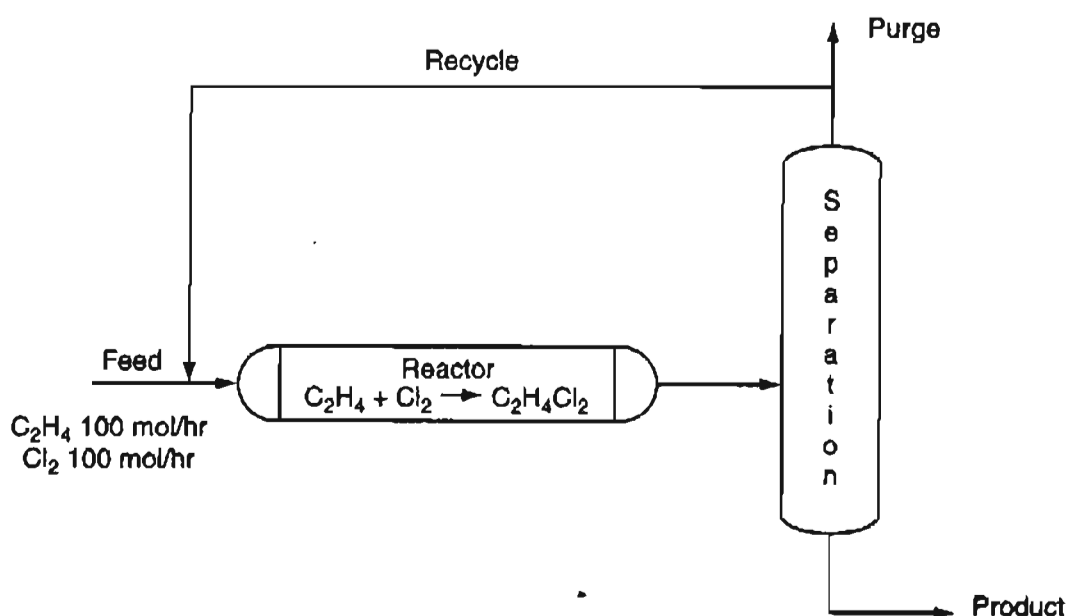


Figure SAT12.4P2

12.5 The Industrial Application of Material Balances

Process simulators, which initially were used for material and energy balances, are now used by process engineers for a number of important activities, including process design, process analysis, and process optimization. *Process design* involves selecting suitable processing units (e.g., reactors, mixers, and distillation columns) and sizing them so that the feed to the process can be efficiently converted into the desired products. *Process analysis* involves comparing predictions of process variables using models of the process units with the measurements made in the operating process. By comparing corresponding values of variables, you can determine if a particular process unit is functioning properly. If discrepancies exist, the predictions from the model can provide insight into the root causes of any problems. In addition, process models can be used to carry out studies that evaluate alternate processing approaches and studies of debottlenecking, that is, methods designed to increase the production rate of the overall process. *Process optimization* is directed at determining the most profitable way to operate the process. For process optimization, models of the major processing units are used to determine the operating conditions, such as product compositions and reactor temperatures, that yield the maximum profit for the process (subject to appropriate constraints).

For each of the three process applications, models of the processing units are based on material balances. For simple equipment, just a few material balances for each component in the system are sufficient to model the equipment. For more complex equipment such as distillation columns, you will find the models involve material balance equations for each component on each tray in a column, and some industrial columns have over 200 trays. For process design and most of process analysis, each processing unit can be analyzed and solved separately. Modern computer codes make it possible to solve extensive sets of simultaneous equations. For example, the optimization model for an ethylene plant usually has over 150,000 equations with material balances comprising over 90% of the equations.

12.5-1 Issues in the Solution of Equations in Models

The simultaneous solution of the large number of equations in process models presents a major challenge for commercial software vendors who develop and maintain the process models used for process design, process analysis, and process optimization. Computational efficiency and solution reliability (including stability and convergence of algorithms) are two important factors affecting the use of commercial process simulators. If an excessive amount of computer time is required to solve the model equations, the utility of the simulators can be seriously undermined, particularly for process optimization applications, because they involve a large number

of equations and naturally require considerable computer time for their solution. Also, optimization applications are applied continuously to many processes so that a long time to achieve a solution, or failure of the algorithm used to solve the equations, seriously degrades the performance of the software, and can make it impossible to obtain any expected benefits.

You should be aware that the computational efficiency and reliability of software are affected by the way in which you formulate the process model equations and the order in which you enter them into the computer. In general, the more linear is a set of model equations, the faster the set can be solved, and the more reliable the solution. You may recall that in Chapter 7 it was pointed out that writing material balances using the mole fractions as unknowns results in a nonlinear set of equations when compared to using the component flow rates. By writing the model equations in **open equation form**, you can improve the computational and reliability achieved by equation solvers for large-scale problems.

Consider system of equations in which a_1 and a_2 are known values:

$$y_1 = a_1 x_1$$

$$y_2 = a_1 x_1 + a_2 x_2$$

Given the values of y_1 and y_2 , the first equation can be used to calculate x_1 . Then the value of x_2 can be calculated using the second equation. This procedure is called the **sequential modular** approach, that is, the equations are solved individually or in relatively small groups, and the results of one set are used to solve for other unknowns in other sets.

The open equation form for the example is written as

$$f_1(x_1, x_2) = y_1 - a_1 x_1$$

$$f_2(x_1, x_2) = y_2 - a_1 x_1 - a_2 x_2$$

By specifying the values of y_1 and y_2 and setting $f_1=f_2=0$, a set of two equations and two unknowns results. The solution to this set of equations is the solution of the original problem. You solve the equations simultaneously for both x_1 and x_2 . This procedure is also called the **simultaneous modular approach**. Both methods yield identical solutions if the computer code is robust to variations in the character of the equation. Why is the open equation form used for industrial-scale model applications? Because it is more computationally efficient and reliable for large-scale problems. The open equation form affords easier development of a standardized model formation so that engineers can combine models and software produced by different programmers without difficulty.

In addition, with the open equation form it is easier to use the same model to calculate various parameters in the equations. For example, for the previous two

equations, given the values of y_1 , y_2 , x_1 , and x_2 , the following equations can be solved to determine the values of a_1 and a_2 .

$$f_1(a_1, a_2) = y_1 - a_1 x_1$$

$$f_2(a_1, a_2) = y_2 - a_1 x_1 - a_2 x_2$$

Note that the equations have not changed, only the known and unknown.

12.5-2 Material Balance Closure for Industrial Processes

One important way in which individual material balances are applied industrially is to check that “in = out,” that is, to determine how well the material balances balance using process measurements in the equations. You look for what is called *closure*, namely that the error between “in” and “out” is acceptable. The flow rates and measured compositions for all the streams entering and exiting a process unit are substituted into the appropriate material balance equations. Ideally, the amount (mass) of each component entering the system should equal the amount of that component leaving the system. Unfortunately, the amount of a component entering a process rarely equals the amount leaving the process when you make such calculations. The lack of closure for material balances on industrial process occurs for several reasons:

1. The process is rarely operating in the steady state. Industrial processes are almost always in a state of flux, and rarely reach precise steady-state behavior.
2. The flow and composition measurements have a variety of errors associated with them. First, sensor readings have noise (variations in the measurement due to more or less random variations in the readings that do not correspond to changes in the process). The sensor readings can also be inaccurate for a wide variety of other reasons. For example, a sensor may require recalibration because it degrades, or it may be used for a measurement for which it was not designed.
3. A component of interest may be generated or consumed inside the process by reactions that the process engineer has not considered.

As a result, material balance closure to within 5% for material balances for most industrial processes is considered reasonable. (Here closure is defined as the calculated difference between the amount of a particular material entering and exiting the process divided by the amount entering multiplied by 100.) If special attention is paid to calibrating sensors, material balance closure of 2 to 3% can be attained. If special high accuracy sensors are used, smaller closure of the material balances can be attained, but if faulty sensor readings are used, much greater errors in material balances are observed. In fact, material balances can be used to determine when faulty sensor readings exist.

Looking Back

Do the words of the jingle at the start of this chapter still apply to you? From the explanation and examples presented in this section you should have concluded that problems involving recycle, purge, and bypass are no different from the viewpoint of how they are analyzed than any of the problems solved in earlier chapters of this book. The one new factor brought out in this chapter is that recycle for a reactor usually involves information about the fraction conversion of a reactant or extent of reaction.

GLOSSARY OF NEW WORDS

By-pass stream A stream that skips one or more units of the process, and goes directly to a downstream unit.

Fresh feed The overall feed to a system.

Gross product The product stream that leaves a reactor.

Once-through fraction conversion The conversion of a reactant based on the amount of material that enters and leaves the reactor.

Open equation form Model equations in which the sum of the terms of each equation represent a deviation from zero.

Overall fraction conversion The conversion of a reactant in a process with recycle based on the fresh feed of the reactant and the overall products.

Overall products The streams that exit a process.

Process feed The feed stream that enters the reactor usually used in a process with a reactor and recycle.

Purge A stream bled off from the process to remove the accumulation of inerts of unwanted material that might otherwise build up in the recycle streams.

Recycle Material (or energy) that leaves a process unit that is downstream and is returned to the same unit or an upstream unit for processing again.

Recycle stream The stream that recycles material.

Recycle system A system that includes one or more recycle streams.

Sequential modular The sequential solution of model equations.

Simultaneous modular Simultaneous solution of model equations.

Single-pass fraction conversion The conversion based on what enters and leave a reactor. See once-through conversion.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent.

Cheremisinoff, P.N., and P. Cheremisinoff. *Encyclopedia of Environmental Control Technology: Waste Minimization and Recycling*, Gulf Publishing, Houston, TX (1992).

Lund, H.F., Ed. *McGraw-Hill Recycling Handbook*, 2nd ed., McGraw-Hill, New York (2000).

Luyben, W.L., and L.A. Wenzel. *Chemical Process Analysis: Mass and Energy Balances*. Intl. Ser. In Phys. & Chem. Engin. Sci, Prentice-Hall, Englewood Cliffs, N.J. (1988).

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Vesilind, P. *Unit Operations in Resource Recovery Engineering*, Prentice-Hall, Upper Saddle River, N.J. (1981).

Web Sites

<http://www.capec.kt.dtu.dk/main/36445/simulators.pdf>

<http://www.dur.ac.uk/a.k.hughes/kpt/module2.html>

<http://www.it.che.wustl.edu/joseph/477/homeworks/>

<http://www.nap.edu/books/0309063779/html/28.html>

PROBLEMS

- *12.1 How many recycle streams exist in each of the following processes?
(a)

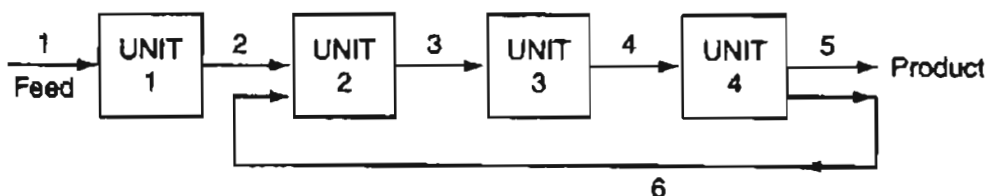


Figure P12.1a

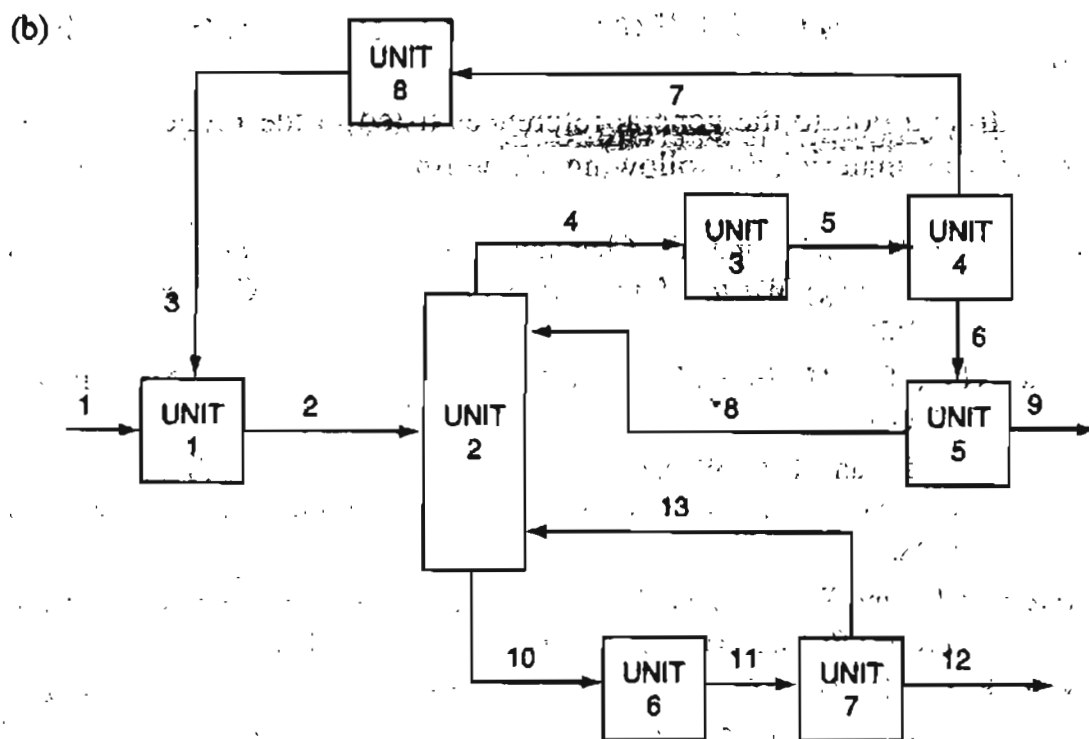


Figure P12.1b

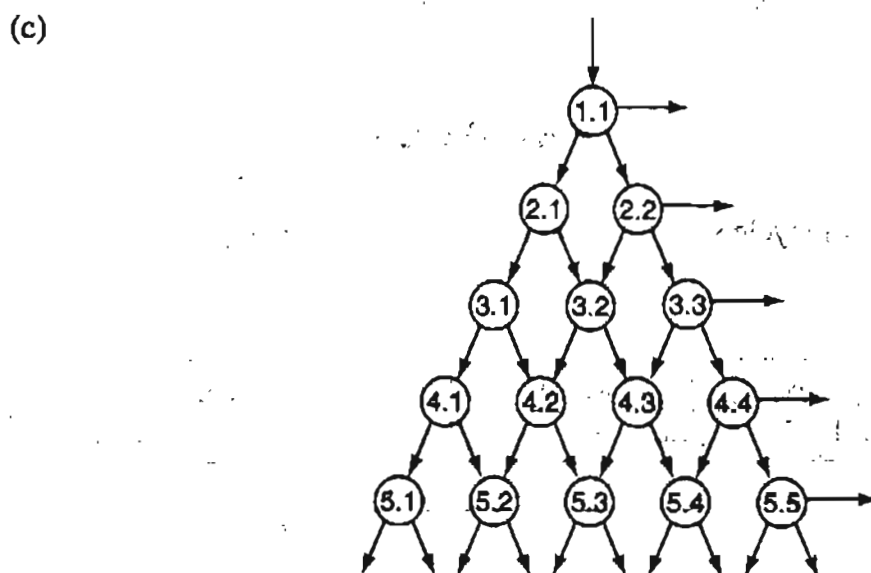


Figure P12.1c

(d)

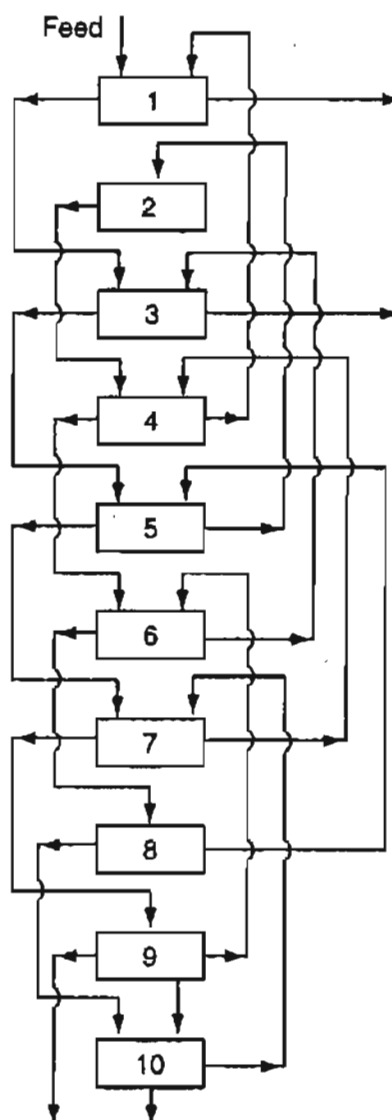


Figure P12.1d

*12.2 Find the kg of recycle/kg feed if the amount of waste (W) is 60 kg of A.

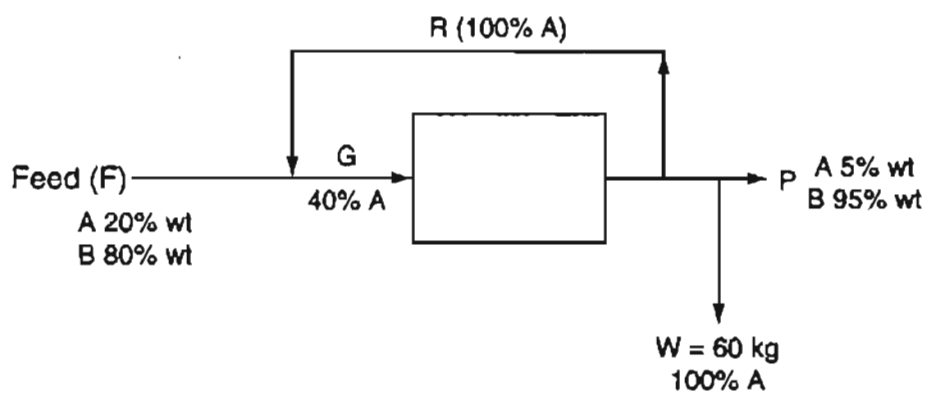


Figure P12.2

*12.3 Find the kg R/100 kg fresh feed.

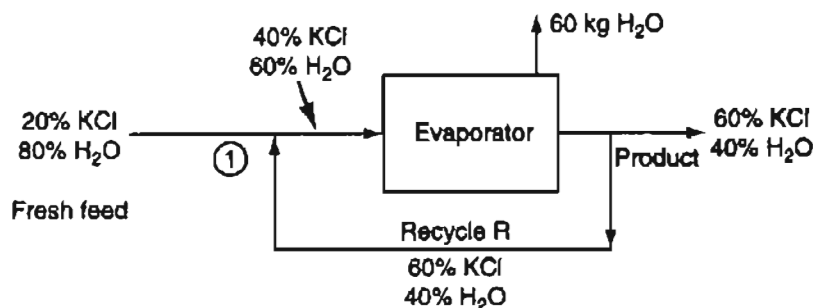


Figure P12.3

*12.4 In the process shown in the Figure P12.4 Unit I is a liquid-liquid solvent extractor and Unit II is the solvent recovery system. For the purposes of designing the size of the pipes for stream C and D, the designer obtained from the given data values of $C = 9,630$ lb/hr and $D = 1,510$ lb/hr. Are these values correct? Be sure to show all details of your calculations or explain if you do not use calculations.

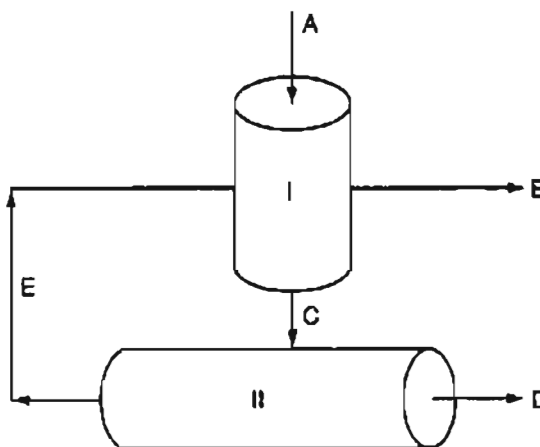


Figure P12.4

Known Data:

	Flow rate (lb/hr)	Composition		
		Butene	Butadiene	Solvent
A	5,000	0.75	0.25	
B			1.00	
C				
D		0.05	0.95	
E	10,000		0.01	0.99

*12.5 The ability to produce proteins through genetic engineering of microbial and mammalian cells and the need for high purity therapeutic proteins has established a need for efficient large scale protein purification schemes.

The system of Continuous Affinity-Recycle Extraction (CARE) combines the advantages of well accepted separation methods, e.g. affinity chromatography, liquid extraction and membrane filtration, while avoiding the drawbacks inherent in batch and column operations.

The technical feasibility of the CARE system was studied using β -galactosidase affinity purification as a test system. Figure P12.5 shows the process. What is the recycle flow rate in mL/hr in each stream? Assume that the concentrations of U are equivalent to the concentrations of the β -galactosidase in solution, and that steady state exists.

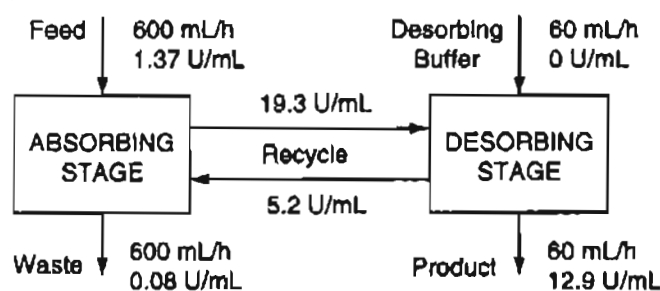


Figure P12.5

- *12.6 Cereal is being dried in a vertical drier by air flowing countercurrent to the cereal. To prevent breakage of the cereal flakes, exit air from the drier is recycled. For each 1000 kg/hr of wet cereal fed to the drier, calculate the input of moist fresh air in kg/hr and the recycle rate in kg/hr.

Data on stream compositions (note some are mass and others mol fractions):

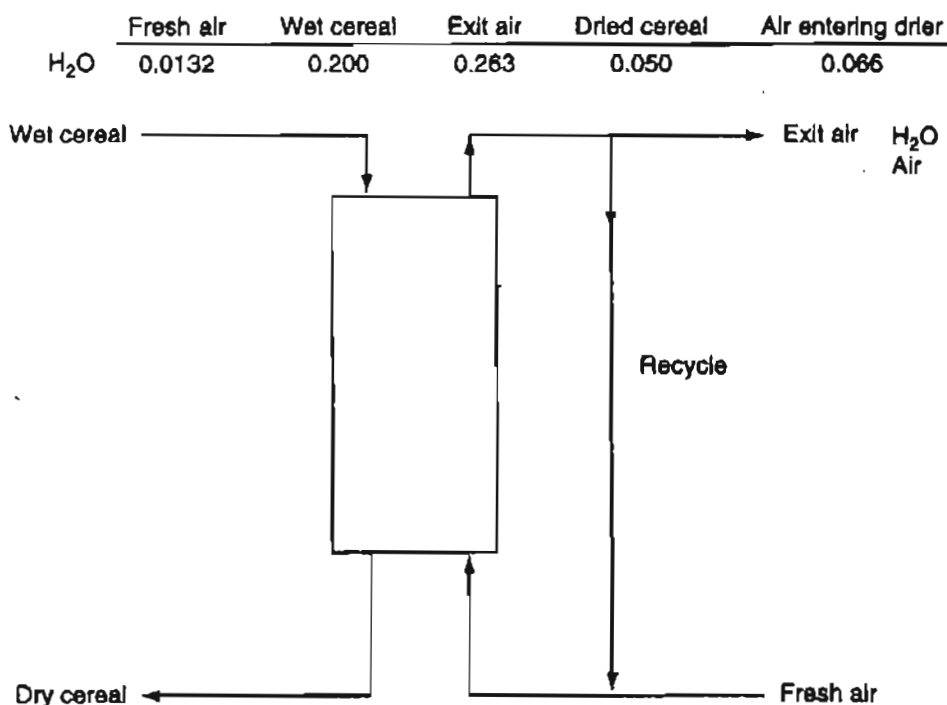


Figure P12.6

- **12.7** Examine Figure P12.7. What is the quantity of the recycle stream in kg/hr? In stream C the composition is 4% water and 96% KNO_3

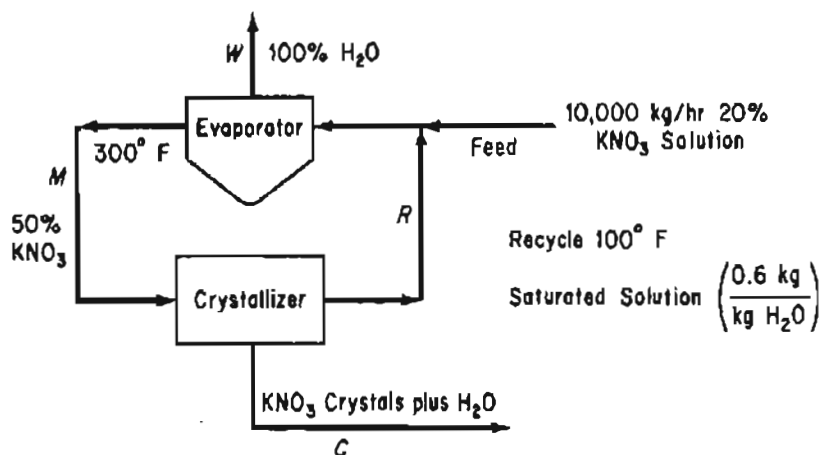


Figure P12.7

- ✓ ****12.8** Sea water is to be desalinated by reverse osmosis using the scheme indicated in Figure P12.8. Use the data given in the figure to determine:
- The rate of waste brine removal (B)
 - The rate of desalinated water (called potable water) production (D)
 - The fraction of the brine leaving the reverse osmosis cell (which acts in essence as a separator) that is recycled.

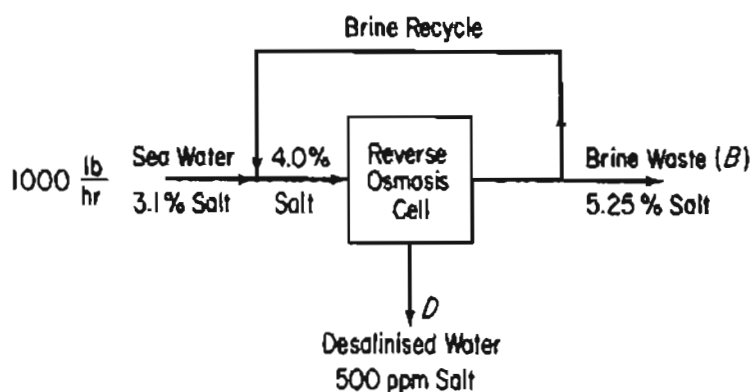


Figure P12.8

- *12.9** A plating plant has a waste stream containing zinc and nickel in quantities in excess of that allowed to be discharged into the sewer. The proposed process to be used as a first step in reducing the concentration of Zn and Ni is shown in Figure P12.9. Each stream contains water. The concentrations of several of the streams are listed in the table. What is the flow (in L/hr) of the recycle stream R_{32} if the feed is 1 L/hr?

Stream	Concentration (g/L)	
	Zn	Ni
F	100	10.0
P ₀	190.1	17.02
P ₂	3.50	2.19
R ₃₂	4.35	2.36
W	0	0
D	0.10	1.00

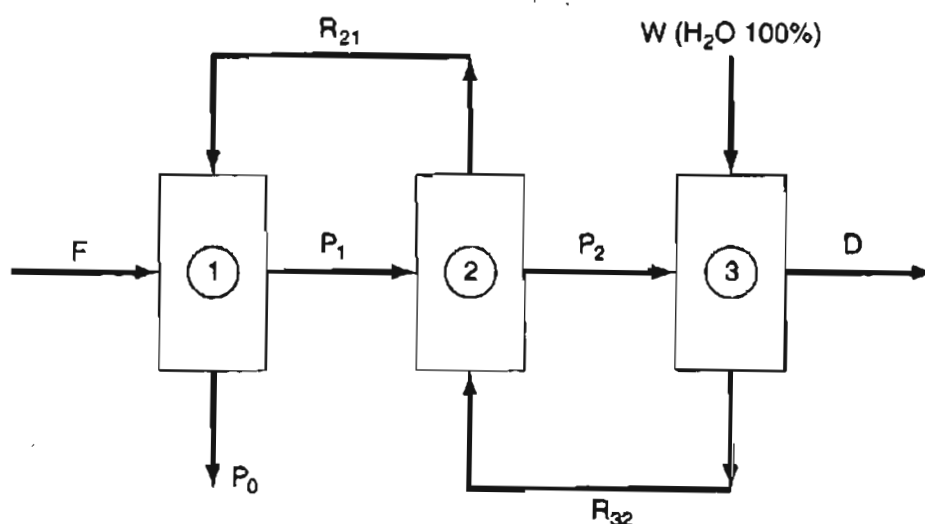


Figure P12.9

****12.10** Ultrafiltration is a method for cleaning up input and output streams from a number of industrial processes. The lure of the technology is its simplicity, merely putting a membrane across a stream to sieve out physically undesirable oil, dirt, metal particles, polymers, and the like. The trick, of course, is coming up with the right membrane. The screening material has to meet a formidable set of conditions. It has to be very thin (less than 1 micron), highly porous, yet strong enough to hold up month after month under severe stresses of liquid flow, pH, particle abrasion, temperature, and other plant operating characteristics.

A commercial system consists of standard modules made up of bundles of porous carbon tubes coated on the inside with a series of proprietary inorganic compositions. A standard module is 6 inches in diameter and contains 151 tubes each 4 feet long with a total working area of 37.5 sq. ft and daily production of 2,000 to 5,000 gallons of filtrate. Optimum tube diameter is about 0.25 inch. A system probably will last at least two to three years before the tubes need replacing from too much residue buildup over the membrane. A periodic automatic chemical cleanout of the tube bundles is part of the system's normal operation. On passing through the filter, the exit stream concentration of oil plus dirt is increased by a factor of 20 over the entering stream.

Calculate the recycle rate in gallons per day (g.p.d.) for the set up shown in Figure P12.10, and calculate the concentration of oil plus dirt in the stream that enters the filtration module. The circled values in Figure P12.10 are the known concentration of oil plus dirt.

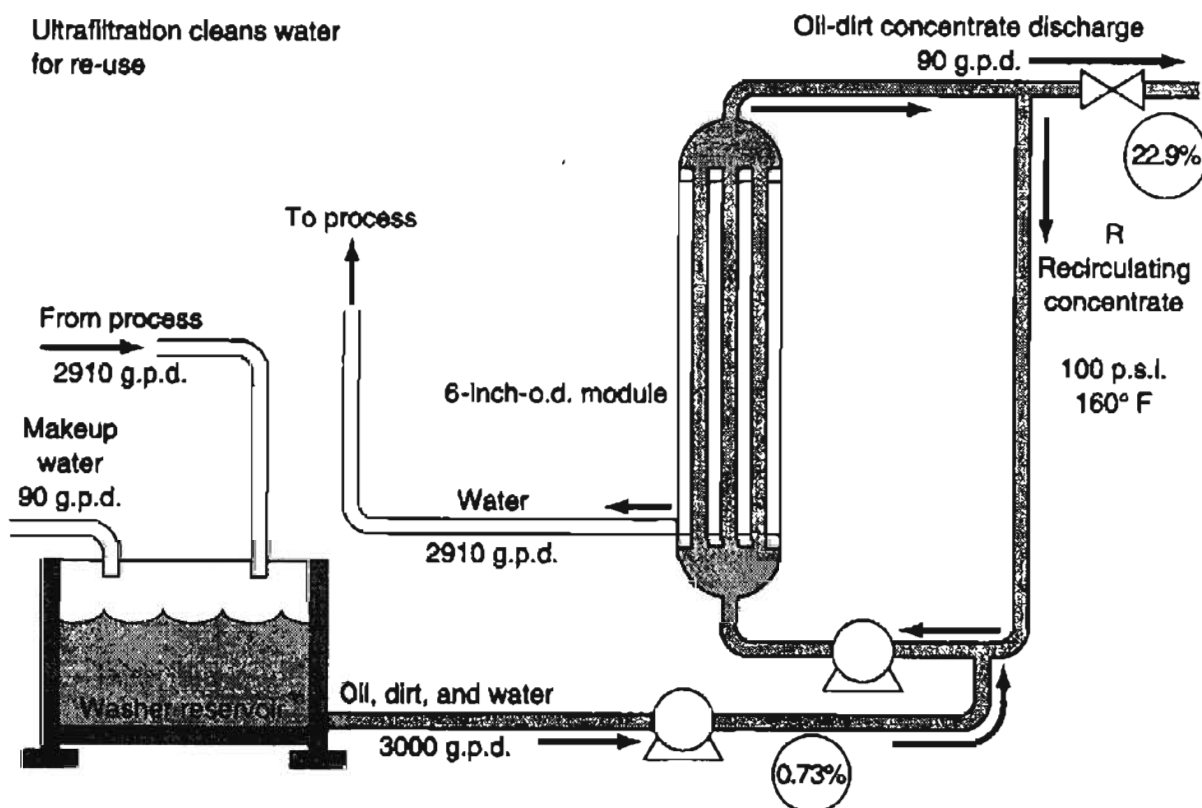


Figure P12.10

- ✓ **12.11 To save energy, stack gas from a furnace is used to dry rice. The flow sheet and known data are shown in Figure P12.11. What is the amount of recycle gas (in lb mol) per 100 lb of P if the concentration of water in the gas stream entering the dryer is 5.20%?

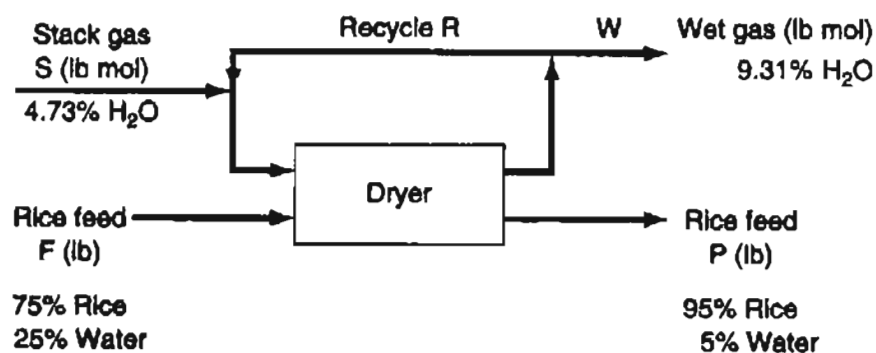


Figure P12.11

- **12.12** This problem is based on the data of G.F. Payne, "Bioseparations of Traditional Fermentation Products" in *Chemical Engineering Problems in Biotechnology*, ed. M.L. Schuler. American Institute of Chemical Engineers, New York: 1989. Examine Figure P12.12. Three separation schemes are proposed to separate the desired fermentation products from the rest of the solution. Ten liters/min of a broth containing 100g/L of undesirable product is to be separated so that the concentration in the exit wastestream is reduced to (not more than) 0.1 g/L. Which of the three flowsheets requires the least fresh pure organic solvent? Ignore any possible density changes in the solutions. Use equal values of the organic solvent in (b), i.e., $F_1^O + F_2^O + F_3^O = F^O$. The relation between the concentration of the undesirable material in the aqueous phase and that in the organic phase is 10 to 1 that is, $c^A/c^O = 10$ in the outlet streams of each unit.

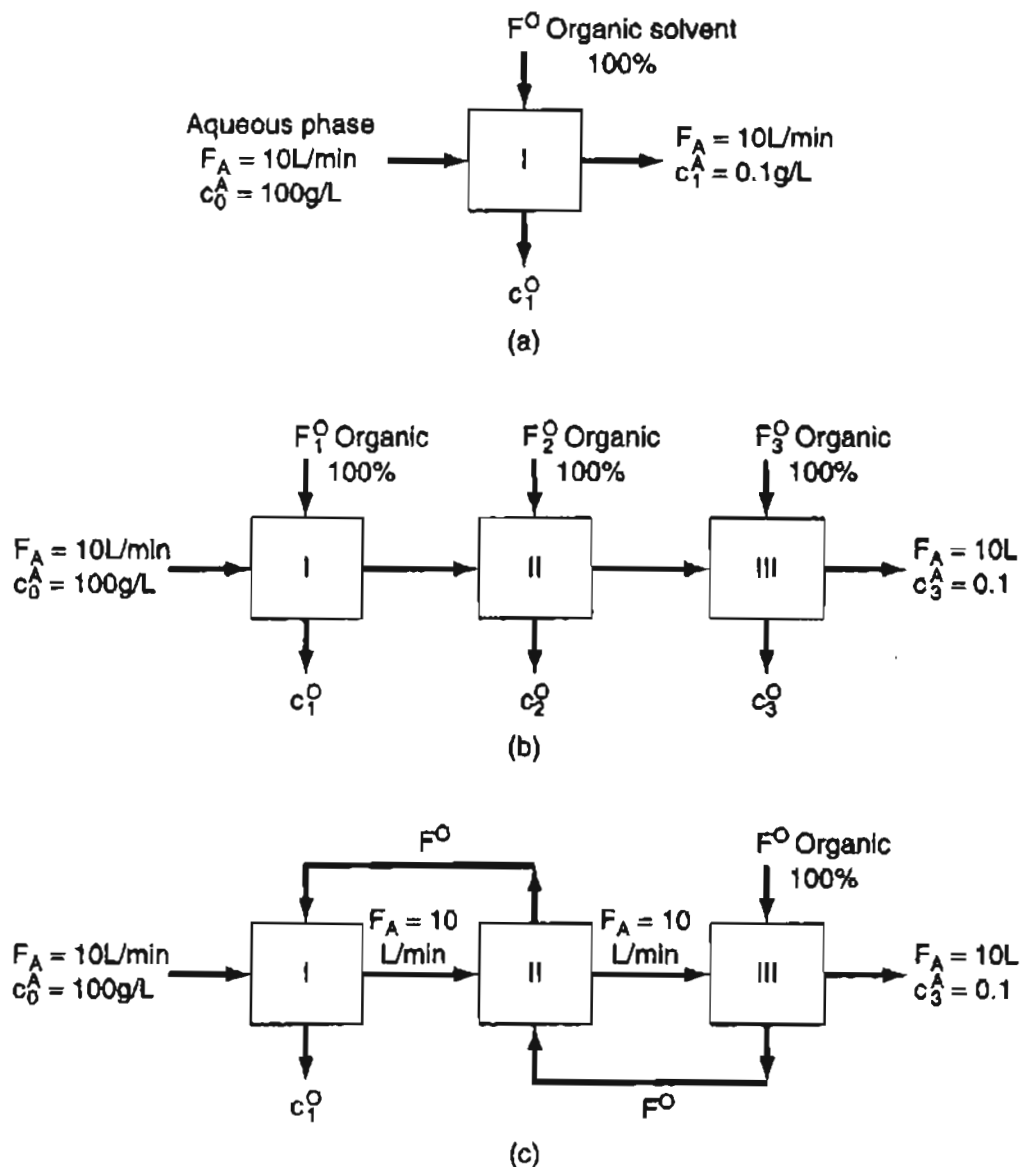


Figure P12.12

*****12.13** Benzene, toluene and other aromatic compounds can be recovered by solvent extraction with sulfur dioxide. As an example, a catalytic reformat stream containing 70% by weight benzene and 30% non-benzene material is passed through the counter-current extractive recovery scheme shown in the diagram in Figure P12.13. One thousand kg of the reformat stream and 3000 kg of sulfur dioxide are fed to the system per hour. The benzene product stream contains 0.15 kg of sulfur dioxide per kg of benzene. The waste stream contains all the initially charged non-benzene material as well as 0.25 kg of benzene per kg of the non-benzene material. The remaining component in the waste stream is the sulfur dioxide.

- (a) How many kg of benzene are extracted per hour (are in the product stream)?
 (b) If 800 kg of benzene containing 0.25 kg of the non-benzene material per kg of benzene are flowing per hour at point A and 700 kg of benzene containing 0.07 kg of the non-benzene material per kg of benzene are flowing at point B, how many kg (exclusive of the sulfur dioxide) are flowing at points C and D?

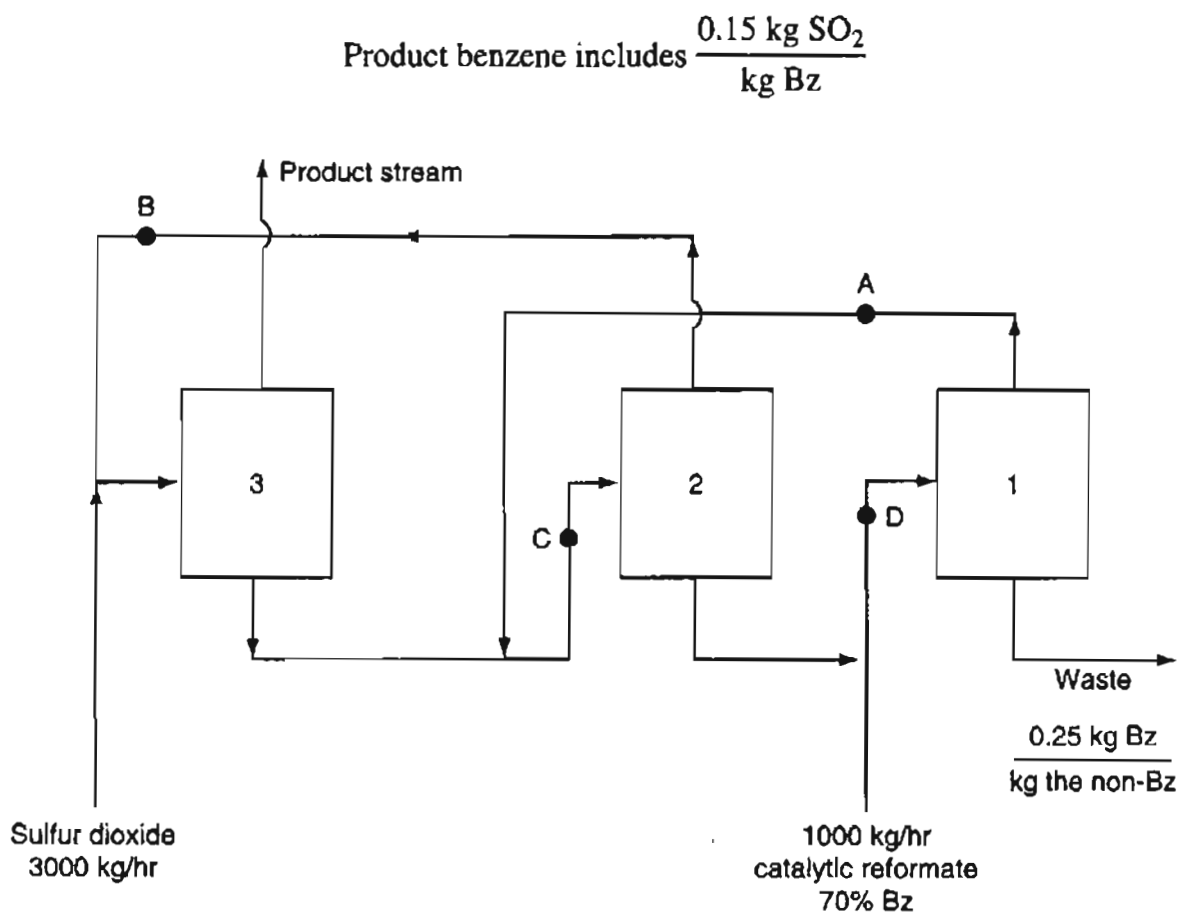


Figure P12.13

***12.14** Examine Figure P12.14 (data for 1 hour).

- What is the single pass conversion of H_2 in the reactor?
- What is the single pass conversion of CO ?
- What is the overall conversion of H_2 ?
- What is the overall conversion of CO ?

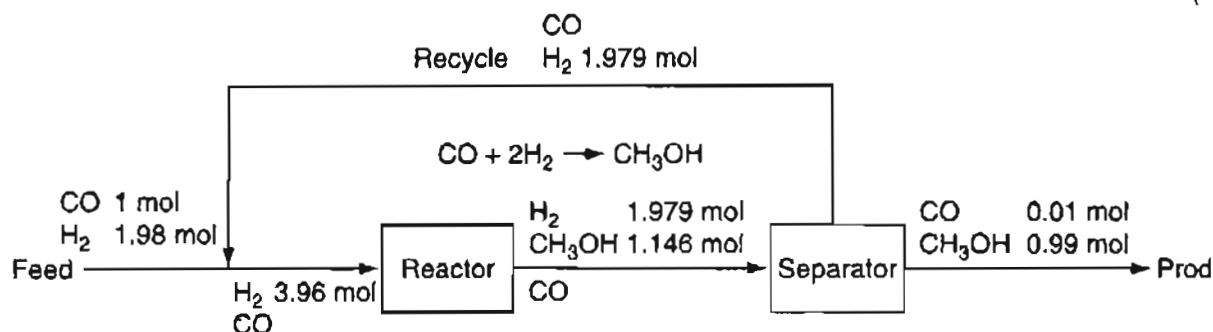
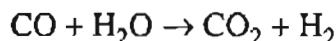


Figure P12.14

*12.15 Hydrogen, important for numerous processes, can be produced by the shift reaction:



In the reactor system shown in Figure P12.15, the conditions of conversion have been adjusted so that the H₂ content of the effluent from the reactor is 3 mole %. Based on the data in Figure P12.5:

- Calculate the composition of the fresh feed.
- Calculate the moles of recycle per mole of hydrogen produced.

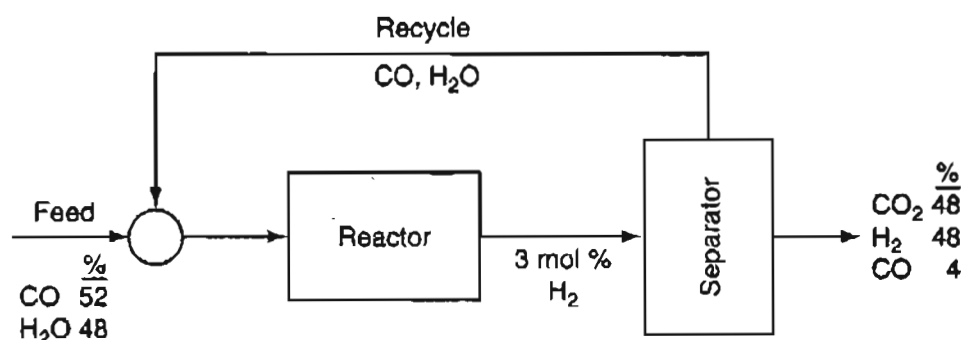


Figure P12.15

*12.16 Acetic acid (HAc) is to be generated by the addition of 10 percent excess sulfuric acid to calcium acetate ($\text{Ca}(\text{Ac})_2$). The reaction $\text{Ca}(\text{Ac})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HAc}$ goes to 90 percent completion based on a single pass through the reactor. The unused $\text{Ca}(\text{Ac})_2$ is separated from the products of the reaction and recycled. The HAc is sep-

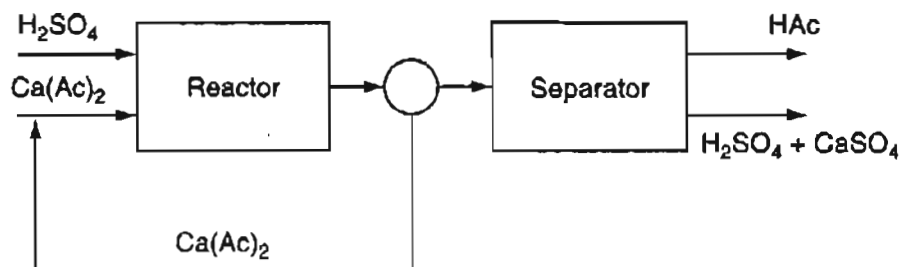


Figure P12.16

arated from the remaining products. Find the amount of recycle per hour based on 1000 kg of $\text{Ca}(\text{Ac})_2$ feed per hour, and also calculate the kg of HAc manufactured per hour. See Figure P12.16 that illustrates the process. ($\text{Ac} = \text{CH}_3\text{CO}_2^-$)

- *12.17 The reaction of ethyl-tetrabromide with zinc dust proceeds as shown in Figure P12.17.

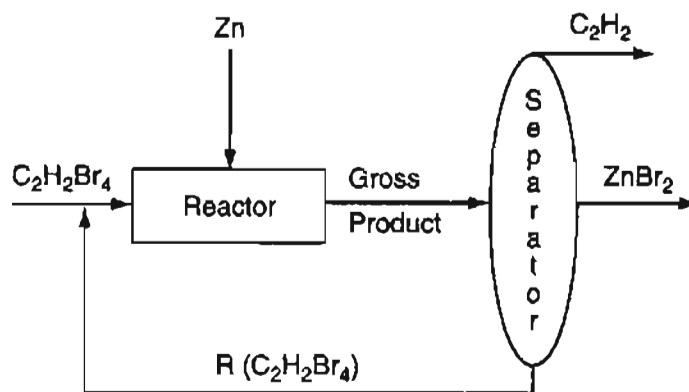


Figure P12.17

The reaction is $\text{C}_2\text{H}_2\text{Br}_4 + 2\text{Zn} \rightarrow \text{C}_2\text{H}_2 + 2\text{ZnBr}_2$. Based on one pass through the reactor, 80% of the $\text{C}_2\text{H}_2\text{Br}_4$ is reacted and the remainder recycled. On the basis of 1000 kg of $\text{C}_2\text{H}_2\text{Br}_4$ fed to the reactor per hour, calculate:

- How much C_2H_2 is produced per hour (in kg)
 - The rate of recycle in kg/hr
 - The feed rate necessary for Zn to be 20% in excess
 - The mole ratio of ZnBr_2 to C_2H_2 in the final products
- *12.18 Examine the accompanying figure. NaCl and the feed solution react to form CaCl_2 . In the reactor the conversion of CaCO_3 is 76% complete. Unreacted CaCO_3 is recycled. Calculate (a) the kg of Na_2CO_3 exiting the separator per 1000 kg of feed, and (b) the kg of CaCO_3 recycled per 1000 kg of feed.

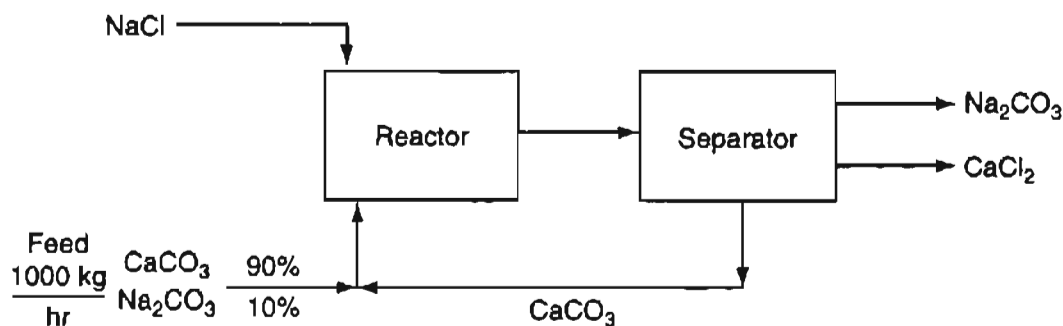
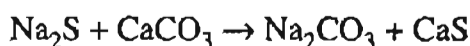


Figure P12.18

- *12.19 In the process sketched below, Na_2CO_3 is produced by the reaction



The reaction is 90% complete on one pass through the reactor and the amount of CaCO_3 entering the reactor is 50% in excess of that needed. Calculate on the basis of 1000 lb/hr of fresh feed:

- the lb of Na_2S recycled, and
- the lb of Na_2CO_3 solution formed per hour.

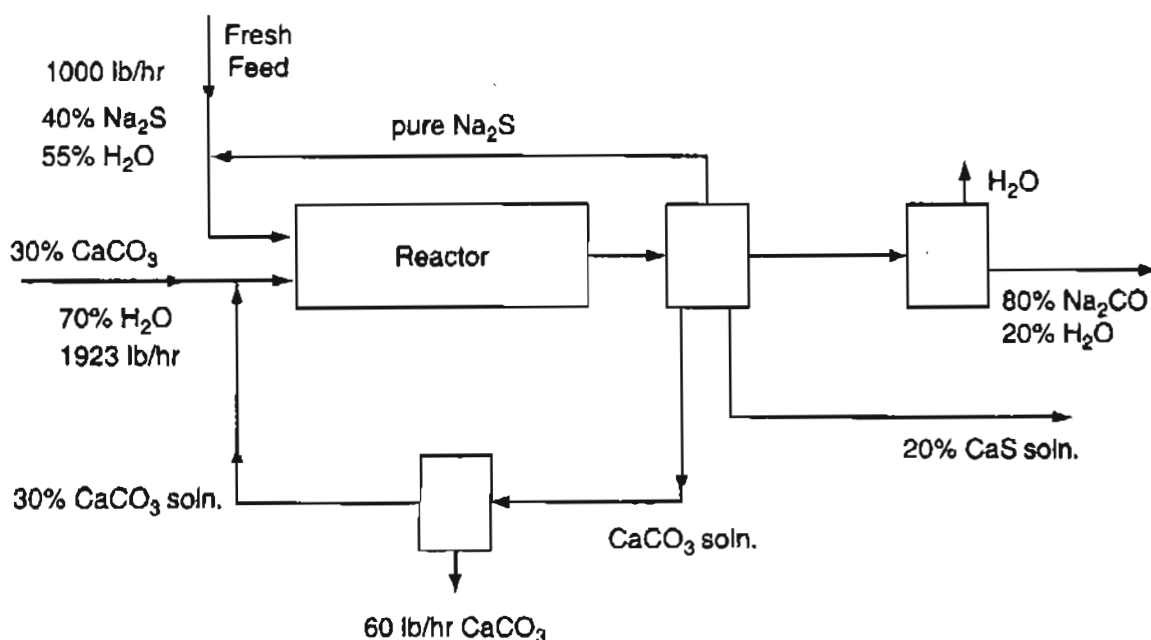
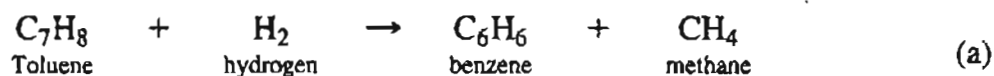


Figure P12.19

- ✓ **12.20** Toluene reacts with H_2 to form benzene (B), but a side reaction occurs in which a by-product diphenyl (D) is formed:



The process is shown in Figure P12.20. Hydrogen is added to the gas recycle stream to make the ratio of H_2 to CH_4 1 to 1 before the gas enters the mixer. The ratio of H_2 to toluene entering the reactor at G is 4H_2 to 1 toluene. The conversion of toluene to benzene on one pass through the reactor is 80%, and the conversion of toluene to the by-product diphenyl is 8% on the same pass.

Calculate the moles of R_G and moles of R_L per hour.

Data:	Compound:	H_2	CH_4	C_2H_6	C_7H_8	$\text{C}_{12}\text{H}_{10}$
	M W:	2	16	78	92	154

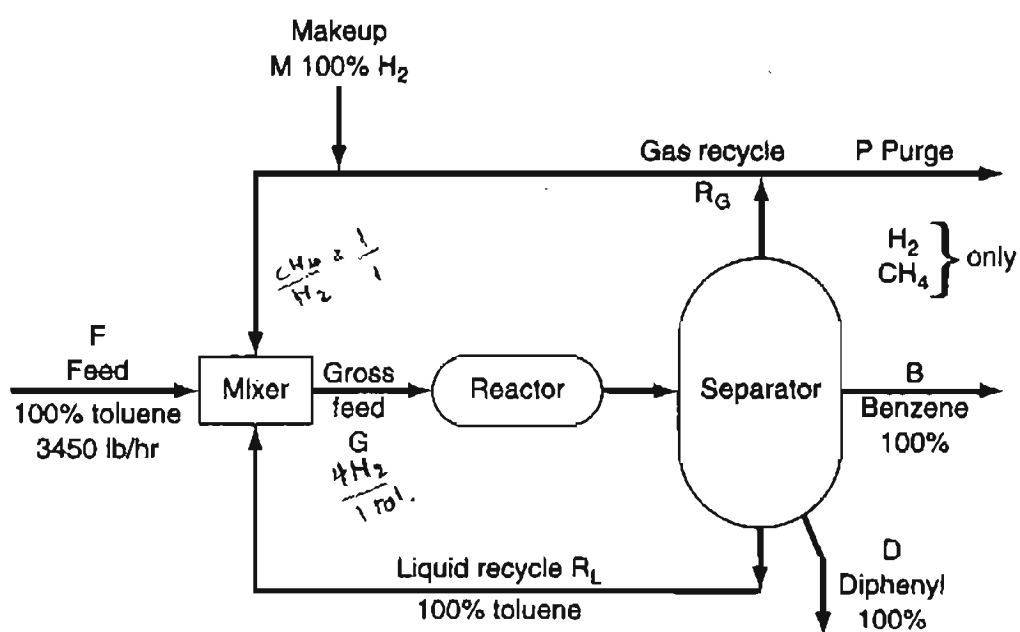
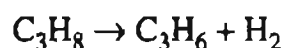


Figure P12.20

- ✓**12.21 The process shown in Figure P12.21 is the dehydrogenation of propane (C₃H₈) to propylene (C₃H₆) according to the reaction



The conversion of propane to propylene based on the *total* propane feed into the reactor at F_2 is 40%. The product flow rate F_5 is 50 kg mol/hr.

- Calculate all the six flow rates F_1 to F_6 in kg mol/hr.
- What is the percent conversion of propane in the reactor based on the fresh propane fed to the process (F_1).

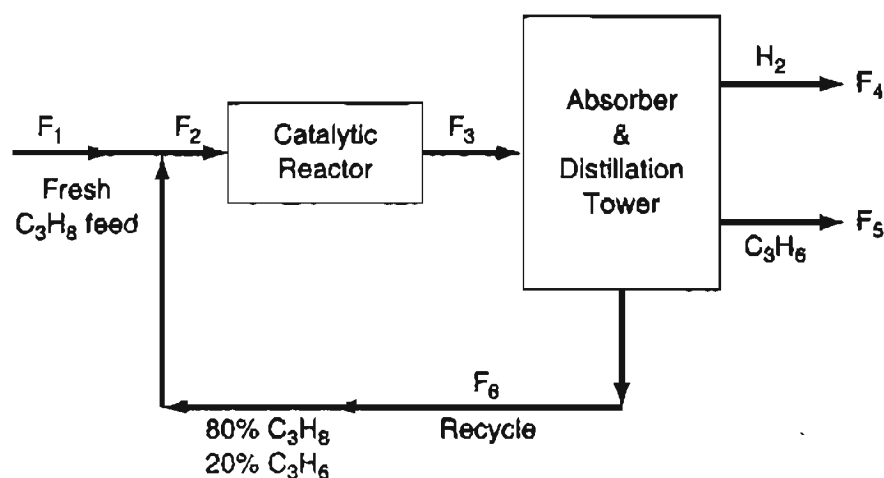


Figure P12.21

****12.22** Natural gas (CH_4) is burned in a furnace using 15% excess air based on the complete combustion of CH_4 . One of the concerns is that the exit concentration of NO (from the combustion of N_2) is about 415 ppm. To lower the NO concentration in the stack gas to 50 ppm it is suggested that the system be redesigned to recycle a portion of the stack gas back through the furnace. You are asked to calculate the amount of recycle required. Will the scheme work? Ignore the effect of temperature on the conversion of N_2 to NO, that is, assume the conversion factor is constant.

****12.23** Sulfur dioxide may be converted to SO_3 , which has many uses including the production of H_2SO_4 and sulphonation of detergent. A gas stream having the composition shown in Figure P12.23 is to be passed through a two-stage converter. The fraction conversion of the SO_2 to SO_3 (on one pass through) in the first stage is 0.75 and in the second stage 0.65. To boost the overall conversion to 0.95, some of the exit gas from stage 2 is recycled back to the inlet of stage 2. How much must be recycled per 100 moles of inlet gas (stream F)? Ignore the effect of temperature on the conversion.

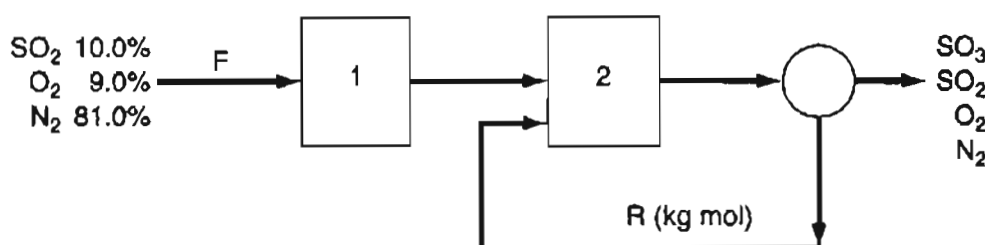
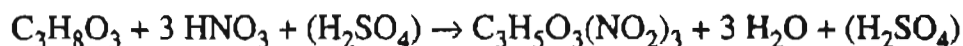


Figure P12.23

*****12.24** Nitroglycerine, a widely used high explosive, when mixed with wood flour is called “dynamite.” It is made by mixing high-purity glycerine (99.9 + percent pure) with nitration acid, which contains 50.00 percent H_2SO_4 , 43.00 percent HNO_3 , and 7.00 percent water by weight. The reaction is:



The sulfuric acid does not take part in the reaction, but is present to “catch” the water formed. Conversion of the glycerine in the nitrator is complete, and there are no side reactions, so all of the glycerine fed to the nitrator forms nitroglycerine. The mixed acid entering the nitrator (Stream G) contains 20.00 percent excess HNO_3 to assure that all the glycerine reacts. Figure P12.24 is a process flow diagram.

After nitration, the mixture of nitroglycerine and spent acid (HNO_3 , H_2SO_4 , and water) goes to a separator (a settling tank). The nitroglycerine is insoluble in the spent acid, and its density is less, so it rises to the top. It is carefully drawn off as product stream P and sent to wash tanks for purification. The spent acid is withdrawn from the bottom of the separator and sent to an acid recovery tank, where the HNO_3 and H_2SO_4 are separated. The H_2SO_4 - H_2O mixture is Stream W, and is concentrated and sold for industrial purposes. The recycle stream to the nitrator is a 70.00% by

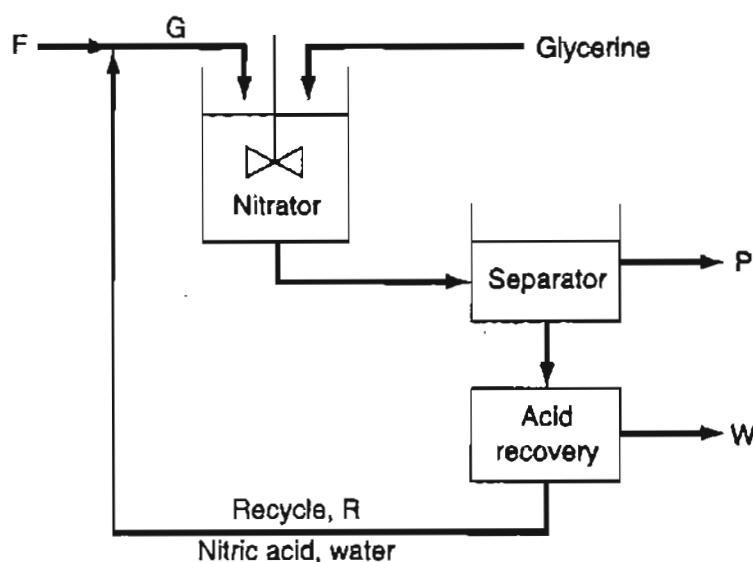


Figure P12.24

weight solution of HNO_3 in water. In the above diagram, product stream P is 96.50% nitroglycerine and 3.50% water by weight.

To summarize:

Stream F = 50.00 wt% H_2SO_4 , 43.00% HNO_3 , 7.00% H_2O

Stream G contains 20.00 percent excess nitric acid

Stream P = 96.50 wt% nitroglycerine, 3.50 wt% water

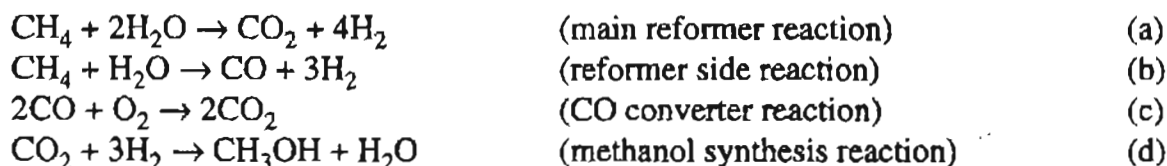
Stream R = 70.00 wt% nitric acid, 30.00% water.

- If 1.000×10^3 kg of glycerine per hour are fed to the nitrator, how many kg per hour of stream P result?
- How many kg per hour are in the recycle stream?
- How many kg of fresh feed, stream F , are fed per hour?
- Stream W is how many kg per hour? What is its analysis in weight percent?

Molecular weights: glycerine = 92.11, nitroglycerine = 227.09, nitric acid = 63.01, sulfuric acid = 98.08, and water = 18.02.

Caution: Do not try this process at home.

- ***12.25** A process for methanol synthesis is shown in Figure P12.25. The pertinent chemical reactions involved are



Ten percent excess steam, based on reaction (a), is fed to the reformer, and conversion of methane is 100%, with a 90% yield of CO_2 . Conversion in the methanol reactor is 55% on one pass through the reactor.

A stoichiometric quantity of oxygen is fed to the CO converter, and the CO is completely converted to CO_2 . Additional makeup CO_2 is then introduced to establish a 3-to-1 ratio of H_2 to CO_2 in the feed stream to the methanol reactor.

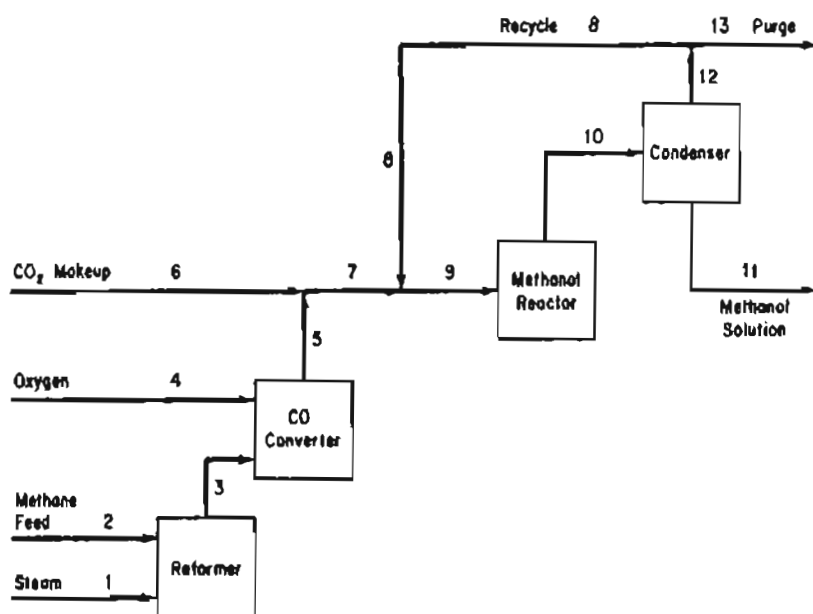


Figure P12.25

The methanol reactor effluent is cooled to condense all the methanol and water, with the noncondensable gases recycled to the methanol reactor feed. The H_2/CO_2 ratio in the recycle stream is also 3-to-1.

Because the methane feed contains 1% nitrogen as an impurity, a portion of the recycle stream must be purged as shown in Figure P12.25 to prevent the accumulation of nitrogen in the system. The purge stream analyzes 5% nitrogen.

On the basis of 100 mol of methane feed (including the N_2), calculate:

- How many moles of H_2 are lost in the purge
- How many moles of makeup CO_2 are required
- The recycle to purge ratio in mol/mol
- How much methanol solution (in kg) of what strength (weight percent) is produced.

*12.26 Alkyl halides are used as an alkylating agent in various chemical transformations. The alkyl halide ethyl chloride can be prepared by the following chemical reaction:

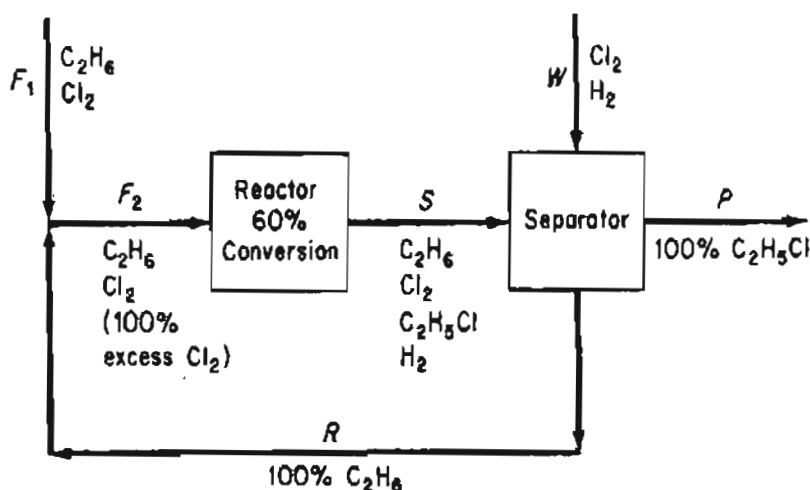
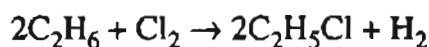


Figure P12.26

In the reaction process shown in Figure P12.26, fresh ethane and chlorine gas and recycled ethane are combined and fed into the reactor. A test shows that if 100% excess chlorine is mixed with ethane, a single-pass optimal conversion of 60% results, and of the ethane that reacts, all is converted to products and none goes into undesired products. You are asked to calculate:

- The fresh feed concentrations required for operation
- The moles of C_2H_5Cl produced in P per mole of C_2H_6 in the fresh feed F_1 .

What difficulties will you discover in the calculations?

- ✓*12.27 Many chemical processes generate emissions of volatile compounds that need to be controlled. In the process shown in Figure P12.27, the exhaust of CO is eliminated by its separation from the reactor effluent and recycling of 100% of the CO generated in the reactor together with some reactant back to the reactor feed.

Although the product is proprietary, information is provided that the feed stream contains 40% reactant, 50% inert, and 10% CO, and that on reaction 2 moles of reactant yield 2.5 moles of product. Conversion of reactant to product is only 73% on one pass through the reactor, and 90% overall. You are asked to calculate the ratio of moles of recycle to moles of product. What do you discover is wrong with this problem?

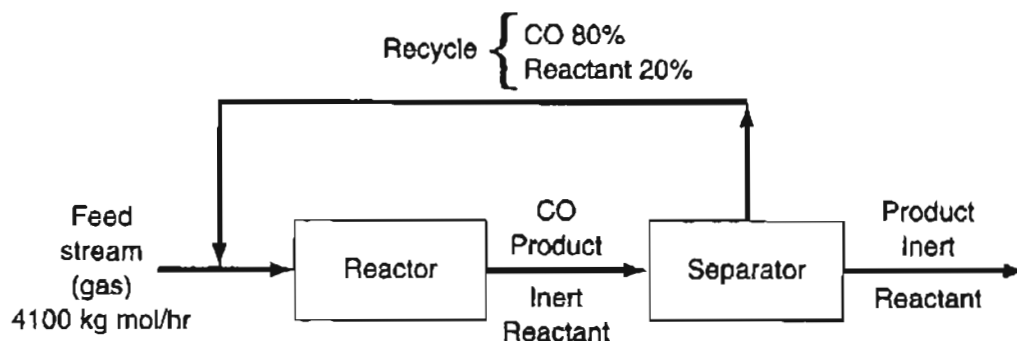


Figure P12.27

- ***P12.28 The following problem is condensed from Example 10.3-1 in the book by D. T. Allen and D. R. Shonnard, *Green Engineering* published by Prentice Hall, Englewood Cliffs, NJ, 2002. Acrylonitrile (AN) can be produced by the reaction of propylene with ammonia in the gas phase

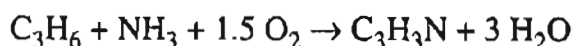


Figure P12.28 is the flowsheet for the process with the data superimposed. The only contaminate of concern is the ammonia.

Answer the following questions.

- Can any of the waste streams that are collected and sent to treatment be used to replace some of the boiler water feed?
- What streams might be considered as candidates to replace some of the feed to the scrubber?

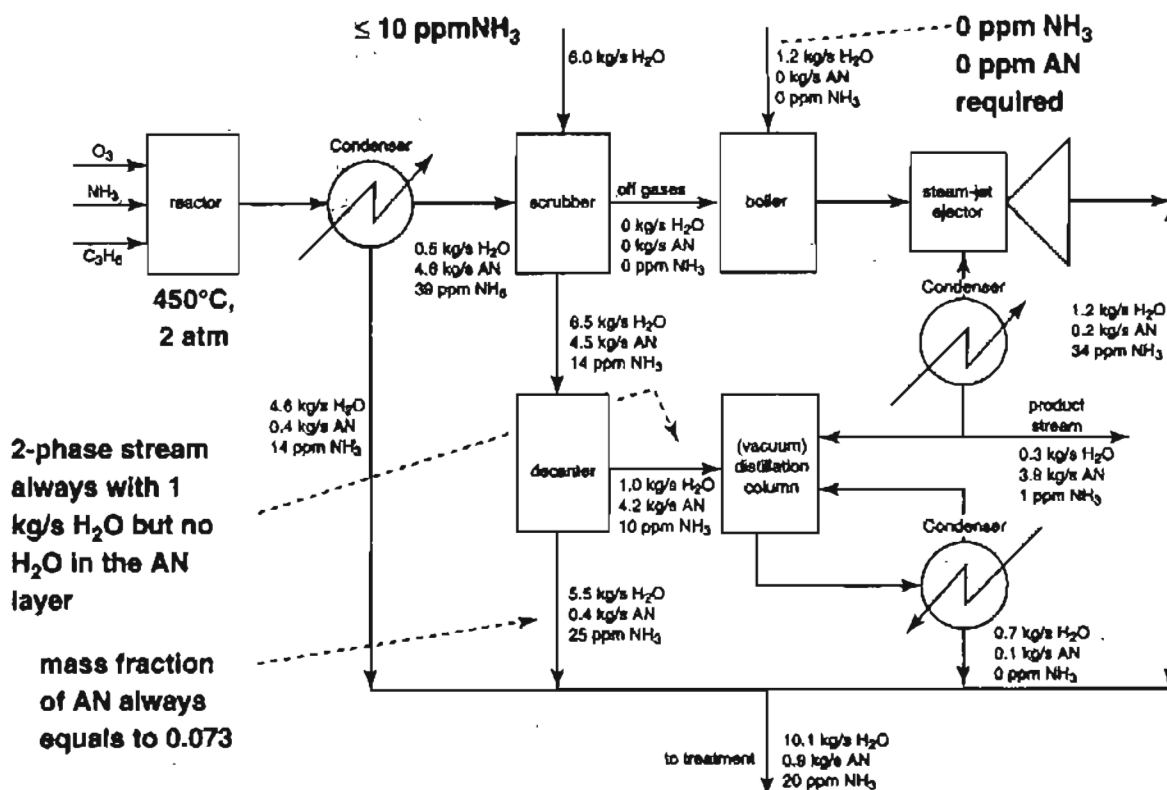


Figure P12.28

- c. If the discharge stream from the condenser associated with the distillation column is recycled back to the scrubber to replace 0.7 kg/s of the water used in the scrubber, what changes in the flows and concentrations will occur in the process?

PART 3

GASES, VAPORS, LIQUIDS, AND SOLIDS

CHAPTER	PAGE
13 Ideal Gases	401
14 Real Gases (Compressibility)	435
15 Real Gases (Equations of State)	459
16 Single Component, Two Phase Systems (Vapor Pressure)	475
17 Two-Phase Gas-Liquid Systems (Saturation Condensation, and Vaporization)	509
18 Two-Phase Gas-Liquid Systems (Partial Saturation and Humidity)	537
19 The Phase Rule and Vapor-Liquid Equilibria	560
20 Liquids and Gases in Equilibrium with Solids	590

We now take up the third prominent topic in this book, how to predict physical properties of pure components and mixtures. By **property** we mean any measurable characteristic of a substance, such as pressure, volume, or temperature, or a characteristic that can be calculated or deduced, such as internal energy, which is discussed in Chapter 21. The **state** of a system is the condition of a system as specified by its properties. You can find values for properties of compounds and mixtures in many formats, including:

1. Experimental data
2. Tables
3. Graphs
4. Equations

as indicated in Figure Part 3A.

You have to become familiar with techniques of correlating and predicting physical properties because values of properties underlie the design, operation, and

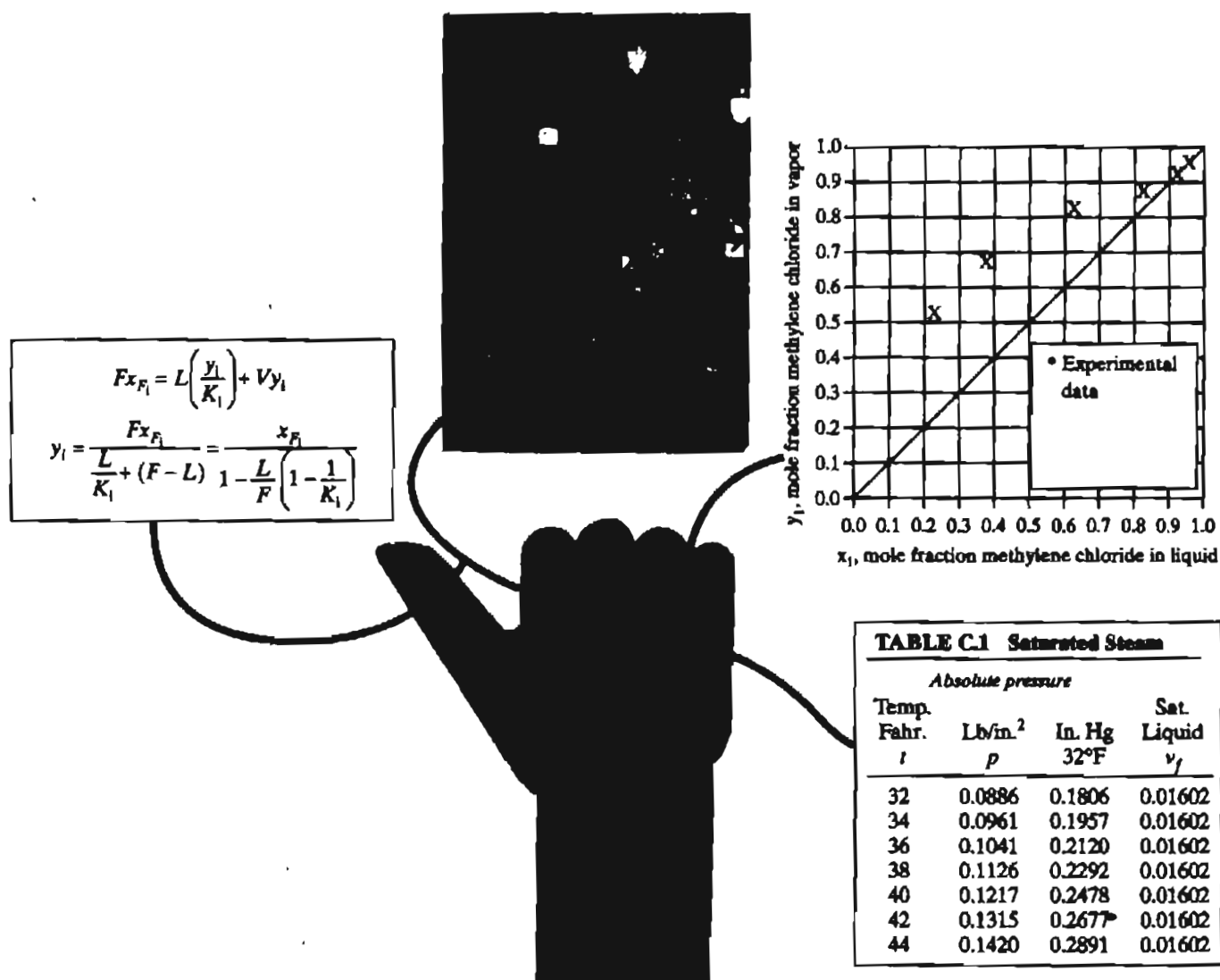


Figure Part 3A Sources of information used to retrieve physical properties.

troubleshooting in all processes. Companies and researchers make a significant investment in collecting data and assessing their validity before storing the data and equations that evolve from data in a data bank—a capital asset.

Not everything that can be counted counts, and not everything that counts can be counted.

Albert Einstein

Clearly you cannot realistically expect to have reliable, detailed experimental data at hand for the properties of all of the useful pure compounds and mixtures with which you will be involved. Consequently, in the absence of experimental information, you have to estimate (predict) properties based on empirical correlations or graphs so that you can introduce appropriate parameters in material and energy

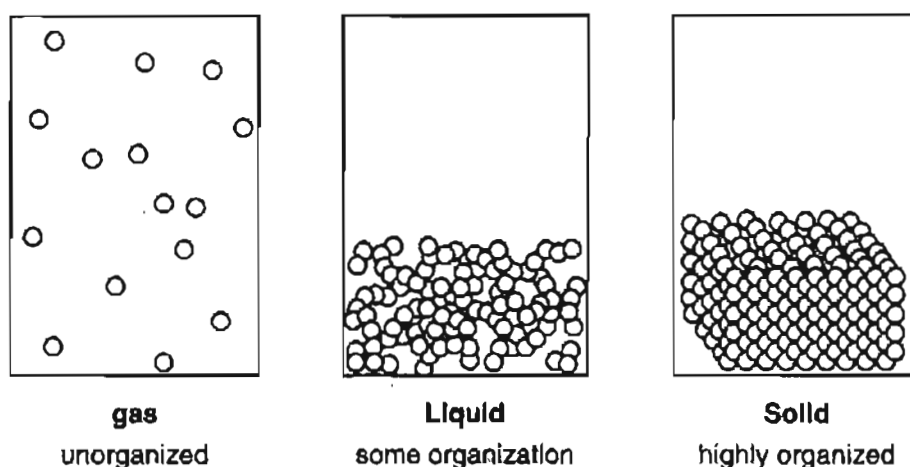


Figure Part 3B Three phases of a compound showing the classification by degree of organization.

balances. The foundation of the estimation methods ranges from quite theoretical to completely empirical, and the reliability of the methods ranges from excellent to terrible.

At any temperature and pressure, a pure compound can exist as a gas, liquid, or solid, and at certain specific values of T and p , mixtures of phases exist, such as when water boils or freezes, as indicated in Figure Part 3B.

Thus, a compound (or a mixture of compounds) may consist of one or more phases. A **phase** is defined as a completely homogeneous and uniform state of matter. Liquid water would be a phase and ice would be another phase. Two immiscible liquids in the same container, such as mercury and water, would represent two different phases because the liquids, although each are homogeneous, have different properties.

In the first chapters we first discuss ideal and real gas relationships. You will learn about methods of expressing the p - V - T properties of real gases by means of equations of state, and, alternatively, by compressibility factors. Next, we introduce the concepts of vaporization, condensation, and vapor pressure, and illustrate how material balances are made for saturated and partially saturated gases. Subsequently, we discuss vapor-liquid relations, and finally examine relations for gases and liquids absorbed on solids.

GLOSSARY OF NEW WORDS

Phase A homogeneous and uniform state of matter, not necessarily continuous.

Property A measurable or calculable characteristic of material.

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CHAPTER 13

IDEAL GASES

13.1 The Ideal Gas Law	402
13.2 Ideal Gas Mixtures and Partial Pressure	412
13.3 Material Balances Involving Ideal Gases	416

Your objectives in studying this chapter are to be able to:

1. Write down the ideal gas law and define all its variables and parameters.
2. Calculate the values and units of the ideal gas law constant R in any set of units from the standard conditions.
3. Convert gas volumes to moles (and mass), and vice versa.
4. Calculate the value of one variable p , V , T , or n , from a given set of values of the other three variables.
5. Calculate the specific gravity of a gas even if the reference condition is not clearly specified.
6. Calculate the density of a gas given its specific gravity.
7. Define and use partial pressure in gas calculations.
8. Show that under certain assumptions the volume fraction equals the mole fraction in a gas.
9. Solve material balances involving gases.

You have been exposed to the concept of the ideal gas in chemistry and physics. Why study ideal gases again? At least two reasons exist. First, the experimental and theoretical properties of ideal gases are far simpler than the corresponding properties of liquids and solids. Second, use of the ideal gas concept is of considerable industrial importance. A review prior to solving material balances involving gases will refresh your memory.

Looking Ahead

In this chapter we explain how the ideal gas law can be used to calculate the pressure, temperature, volume, or number of moles in a quantity of gas, and define the partial pressure of a gas in a mixture of gases. We also discuss how to calculate the specific gravity and density of a gas. Then we apply the concepts to solving material balances.

13.1 The Ideal Gas Law

In July 1984 an explosion killed a forklift operator in the Port of Houston while he was unloading canisters containing aluminum phosphide (a pesticide) from a Brazilian ship. The Coast Guard later discovered that the batch of pesticide, which was stored in a nitrogen-cooled van, had begun heating up and destabilizing, causing a risk of explosion. They decided to dispose of all of the cylinders by dumping them in the ocean. The chemical becomes poisonous phosphine gas when it contacts air or water.

Initially the canisters containing the pellets simply were unplugged and tossed into the Gulf. After sinking a hundred feet or so, the chemical began reacting on contact with the sea water, and the gas trapped in each bottle forced them back to the surface, where the canister bobbed up and down on the waves. The Coast Guard issued rifles to sharpshooters to blast each canister before it drifted dangerously away. "It was a carnival" said a local federal legislator in disgust. If you had been consulted about the disposal of the cylinders, could you have predicted the outcome? What might you have done? What about applying the ideal gas law to determine how much gas might be generated and act as a propellant to drive a cylinder through the water?

Certainly the most famous and widely used equation that relates p , V , and T for a gas is the **ideal gas law**

$$pV = nRT \quad (13.1)$$

where p = **absolute pressure** of the gas

V = total volume occupied by the gas

n = number of moles of the gas

R = ideal (universal) gas constant in appropriate units

T = **absolute temperature** of the gas

You can find values of R in various units inside the front cover of this book. Sometimes the ideal gas law is written as

$$p\hat{V} = RT \quad (13.1a)$$

where in the equation \hat{V} is the specific molar volume (volume per mole) of the gas. When gas volumes are involved in a problem, \hat{V} will be the volume per mole and not the volume per mass. Figure 13.1 illustrates the surface generated by Equation (13.1a) in terms of the three properties p , \hat{V} , and T . Look at the projections of the surface in Figure 13.1 onto the three two-parameter planes. The interpretation is as follows:

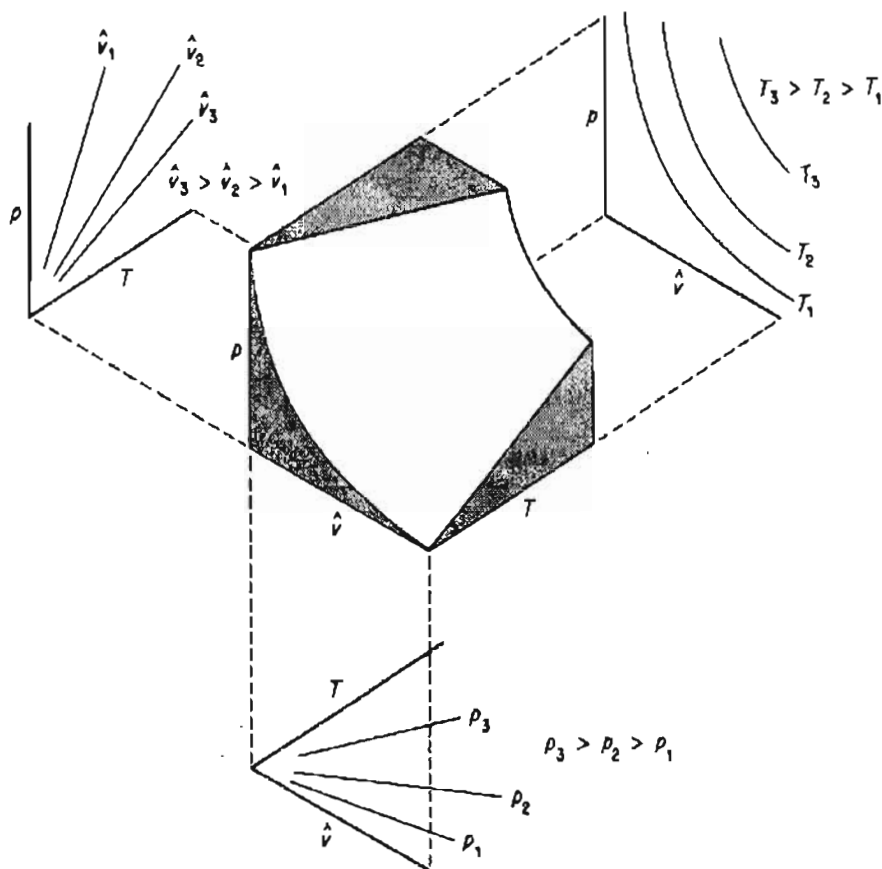


Figure 13.1 Representation of the ideal gas law in three dimensions as a surface.

1. The projection to the left onto the $p - T$ plane shows straight lines for constant values of \hat{V} . Why? Equation (13.1a) for constant specific volume is $p = (\text{constant}) T$, the equation of a straight line.
2. The projection to the right onto the $p - \hat{V}$ plane shows curves for values of constant T . What kinds of curves are they? For constant T , Equation (13.1a) becomes $p\hat{V} = \text{constant}$, namely a hyperbola.
3. The projection downward onto the $T - \hat{V}$ plane again shows straight lines. Why? Equation (13.1a) for constant p is $\hat{V} = (\text{constant}) T$.

Equation (13.1) can be applied to a pure component or to a mixture.

What are the conditions for a gas to behave as predicted by the ideal gas law? The major ones are

1. The molecules of an ideal gas do not occupy any space; they are infinitesimally small.
2. No attractive forces exist between the molecules so that the molecules move completely independently of each other.
3. The gas molecules move in random, straight-line motion, and the collisions between the molecules, and between the molecules and the walls of the container, are perfectly elastic.

Gases at low pressure and/or high temperature meet these conditions. Solids, liquids, and gases at high density, that is, high pressure and/or low temperature, do not. From a practical viewpoint within reasonable error, you can treat air, oxygen, nitrogen, hydrogen, carbon dioxide, methane, and even water vapor under most of the ordinary conditions you encounter as ideal gases.

Several arbitrarily specified standard states (usually known as **standard conditions**, or S.C. or S.T.P. for standard temperature and pressure) of temperature and pressure have been specified for gases by custom. Refer to Table 13.1 for the most

TABLE 13.1 Common Standard Conditions for the Ideal Gas

System	T	P	\hat{V}
SI	273.15K	101.325 kPa	22.415m ³ /kg mol
Universal scientific	0.0°C	760 mm Hg	22.415 liters/g mol
Natural gas industry	59.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft ³ /lb mol
American engineering	491.67°R (32°F)	1 atm	359.05 ft ³ /lb mol

common ones. The fact that a substance cannot exist as a gas at 0°C and 1 atm is immaterial. Thus, as we see later, water vapor at 0°C cannot exist at a pressure greater than its vapor pressure of 0.61 kPa (0.18 in. Hg) without condensation occurring. However, you can calculate the imaginary volume at standard conditions, and it is just as useful a quantity in the calculation of volume–mole relationships as though it could exist. In what follows, the symbol V will stand for total volume and the symbol \hat{V} for volume per mole.

Because the SI, Universal Scientific, and AE standard conditions are identical, you can use the values in Table 13.1 with their units to change from one system of units to another. If you learn the standard conditions, you will find it easy to work with mixtures of units from different systems.

The following example illustrates how you can use the standard conditions to convert mass or moles to volume. After reading it, see if you can explain how to convert volume to moles or mass.

EXAMPLE 13.1 Use of Standard Conditions to Calculate Volume from Mass

Calculate the volume, in cubic meters, occupied by 40 kg of CO₂ at standard conditions assuming CO₂ acts as an ideal gas.

SolutionBasis: 40 kg of CO₂

$$\frac{40 \text{ kg CO}_2}{44 \text{ kg CO}_2} \left| \frac{1 \text{ kg mol CO}_2}{1 \text{ kg mol CO}_2} \right| \frac{22.42 \text{ m}^3 \text{ CO}_2}{1 \text{ kg mol CO}_2} = 20.4 \text{ m}^3 \text{ CO}_2 \text{ at S.C.}$$

Notice in this problem how the information that 22.42 m³ at S.C. = 1 kg mol is applied to transform a known number of moles into an equivalent number of cubic meters. An alternate way to calculate the volume at standard conditions is to use Equation (13.1).

Incidentally, whenever you use volumetric measure, you must establish the conditions of temperature and pressure at which the volumetric measure exists, since the term "m³" or "ft³," standing alone, is really not any particular *quantity* of material.

You can apply the ideal gas law, Equation (13.1), directly by introducing values for three of the four quantities, n , p , T , and V , and solve for the fourth. To do so, you need to look up or calculate R in the proper units. Inside the front cover of this book you will find selected values of R for different combinations of units. Example 13.2 illustrates how to calculate the value of R in any set of units you want from the values of p , T , and \hat{V} at standard conditions.

EXAMPLE 13.2 Calculation of R Using the Standard Conditions

Find the value for the universal gas constant R to match the following combination of units: For 1 g mol of ideal gas when the pressure is in atm, the volume is in cm³, and the temperature is in K.

Solution

The following values are the ones to use (along with their units).
At standard conditions:

$$p = 1 \text{ atm}$$

$$\hat{V} = 22,415 \text{ cm}^3/\text{g mol}$$

$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273.15 \text{ K}} \left| \frac{22,415 \text{ cm}^3}{1 \text{ g mol}} \right| = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

In many processes going from an initial state to a final state, you will find it convenient to use the ratio of the ideal gas laws in the respective states, and thus eliminate R as follows (the subscript 1 designates the initial state, and the subscript 2 designates the final state)

$$\frac{p_1 V_1}{p_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$$

or

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right) \quad (13.2)$$

Note that Equation (13.2) involves ratios of the same variable. This result has the convenient feature that the pressures may be expressed in any system of units you choose, such as kPa, in. Hg, mm Hg, atm, and so on, as long as the same units are used for both conditions of pressure (do not forget that the pressure must be *absolute* pressure in both cases). Similarly, the ratio of the *absolute* temperatures and ratio of the volumes results in ratios that are dimensionless. Note how the ideal gas constant R is eliminated in taking the ratios.

Let's see how you can apply the ideal gas law both in the form of Equation (13.2) and Equation (13.1) to problems.

EXAMPLE 13.3 Application of the Ideal Gas Law to Calculate a Volume

Calculate the volume occupied by 88 lb of CO_2 at 15°C and a pressure of 32.2 ft of water.

Solution

Examine Figure E13.3. To use Equation (13.2) the initial volume has to be calculated as

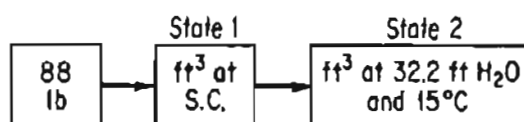


Figure E13.3

shown in Example 13.1. Then the final volume can be calculated via Equation (13.2) in which both R and (n_1/n_2) cancel out:

$$V_2 = V_1 \left(\frac{p_1}{p_2} \right) \left(\frac{T_2}{T_1} \right)$$

Assume that the given pressure is absolute pressure.

At S.C. (state 1)

At (state 2)

$p = 33.91 \text{ ft H}_2\text{O}$

$p = 32.2 \text{ ft H}_2\text{O}$

$T = 273 \text{ K}$

$T = 273 + 15 = 288 \text{ K}$

Basis: 88 lb of CO_2

$$\frac{88 \text{ lb CO}_2}{\frac{44 \text{ lb CO}_2}{1 \text{ lb mol CO}_2}} \times \frac{359 \text{ ft}^3}{1 \text{ lb mol}} \times \frac{288}{273} \times \frac{33.91}{32.2} = 798 \text{ ft}^3 \text{ CO}_2 \text{ at } 32.2 \text{ ft H}_2\text{O and } 15^\circ\text{C}$$

Calculation of V_1

You can mentally check your calculations by saying to yourself: The temperature goes up from 0°C at S.C. to 15°C at the final state, hence the volume must increase from S.C., hence the temperature ratio must be greater than unity. Similarly, you can say: The pressure goes down from S.C. to the final state, so that the volume must increase from S.C., hence the pressure ratio must be greater than unity.

The same result can be obtained by using Equation (13.1). First obtain the value of R in the same units as the variables p , V , and T . Look it up or calculate the value from p , \hat{V} , and T at S.C.

$$R = \frac{p\hat{V}}{T}$$

At S.C.,

$p = 33.91 \text{ ft H}_2\text{O}$ $\hat{V} = 359 \text{ ft}^3/\text{lb mol}$ $T = 273 \text{ K}$

$$R = \frac{33.91}{273} \times \frac{359}{1} = 44.59 \frac{(\text{ft H}_2\text{O})(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

Now, using Equation (13.1), insert the given values, and perform the necessary calculations

Basis: 88 lb of CO_2

$$V = \frac{nRT}{p} = \frac{88 \text{ lb CO}_2}{\frac{44 \text{ lb CO}_2}{1 \text{ lb mol CO}_2}} \times \frac{44.59 (\text{ft H}_2\text{O})(\text{ft}^3)}{(\text{lb mol})(\text{K})} \times \frac{288 \text{ K}}{32.2 \text{ ft H}_2\text{O}}$$

$$= 798 \text{ ft}^3 \text{ CO}_2 \text{ at } 32.2 \text{ ft H}_2\text{O and } 15^\circ\text{C}$$

If you will inspect both solutions closely, you will observe that in both cases the same numbers appear, and that the results are identical.

To calculate the volumetric flow rate of a gas through a pipe, you divide the volume of the gas passing through the pipe in a time interval such as 1 second by the value of the time interval to get m^3/s or ft^3/s . To get the velocity, v , of the flow, you divide the volumetric flow rate by the area, A , of the pipe

$$\dot{V} = A\nu \quad \text{hence } \nu = \dot{V}/A \quad (13.3)$$

The **density of a gas** is defined as the mass per unit volume and can be expressed in kilograms per cubic meter, pounds per cubic foot, grams per liter, or other units. Inasmuch as the mass contained in a unit volume varies with the temperature and pressure, as we have previously mentioned, you should always be careful to specify these two conditions in calculating density. If not otherwise specified, the densities are presumed to be at S.C.

EXAMPLE 13.4 Calculation of Gas Density

What is the density of N_2 at 27°C and 100 kPa in SI units?

Solution

Basis: 1 m^3 of N_2 at 27°C and 100 kPa

$$\frac{1 \text{ m}^3}{1 \text{ m}^3} \left| \frac{273 \text{ K}}{300 \text{ K}} \right| \left| \frac{100 \text{ kPa}}{101.3 \text{ kPa}} \right| \left| \frac{1 \text{ kg mol}}{22.4 \text{ m}^3} \right| \left| \frac{28 \text{ kg}}{1 \text{ kg mol}} \right| = 1.123 \text{ kg}$$

density = 1.123 kg/m^3 of N_2 at 27°C (300K) and 100 kPa

The **specific gravity** of a gas is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure. The use of specific gravity occasionally may be confusing because of the sloppy manner in which the values of specific gravity are reported in the literature. You must be very careful in using literature values of the specific gravity to ascertain that the conditions of temperature and pressure are known both for the gas in question and for the reference gas. Thus, this question is not well posed: *What is the specific gravity of methane?* This question may have the same answer as the question: How many grapes are in a bunch? Unfortunately, occasionally one may see this question and the best possible answer is

$$\text{sp gr} = \frac{\text{density of methane at SC.}}{\text{density of air at S.C.}}$$

in which the temperature and pressure of the methane and reference air are clearly specified.

EXAMPLE 13.5 Calculation of the Specific Gravity of a Gas

What is the specific gravity of N_2 at 80°F and 745 mm Hg compared to air at 80°F and 745 mm Hg?

Solution

One way to solve the problem is to calculate the densities of N_2 and air at their respective conditions of temperature and pressure, and then calculate the specific gravity by taking a ratio of their densities. Example 13.4 covers the calculation of the density of a gas, and therefore, to save space, no units will appear in the intermediate calculation here:

Basis: 1 ft³ of air at 80°F and 745 mm Hg

$$\frac{1}{540} \left| \frac{492}{760} \right| \frac{745}{359} \left| \frac{29}{359} \right| = 0.0721 \text{ lb/ft}^3 \text{ at } 80^\circ\text{F and 745 mm Hg}$$

Basis: 1 ft³ of N_2 at 80°F and 745 mm Hg

$$\frac{1}{540} \left| \frac{492}{760} \right| \frac{745}{359} \left| \frac{28}{359} \right| = 0.0697 \text{ lb/ft}^3 \text{ at } 80^\circ\text{F and 745 mm Hg}$$

$$(\text{sp gr})_{N_2} = \frac{0.0697}{0.0721} = 0.967 \frac{\text{lb } N_2/\text{ft}^3 \text{ at } 80^\circ\text{F, 745 mm Hg}}{\text{lb air/ft}^3 \text{ air at } 80^\circ\text{F, 745 mm Hg}}$$

Did you note from Example 13.5 that for a gas and reference at the *same* temperature and pressure, the specific gravity is just the ratio of the respective molecular weights? You can derive this result as follows. Let A be one gas and B be another. Keep in mind that \hat{V} for a gas is the volume per mole and not the volume per mass.

$$p\hat{V} = RT \quad \text{or} \quad \hat{V} = \frac{1}{\rho/\text{MW}} = [RT/p]$$

Thus

$$\rho = \frac{(p)(\text{MW})}{RT}$$

$$\text{sp gr} = \frac{\rho_A}{\rho_B} = \left(\frac{\text{mol. wt}_A}{\text{mol. wt}_B} \right) \left(\frac{T_B}{T_A} \right) \left(\frac{p_A}{p_B} \right) \quad (13.3)$$

and at the same temperature and pressure for A and B the specific gravity is just the ratio of the respective molecular weights.

SELF-ASSESSMENT TEST

Questions

1. What is the ideal gas law? Write it down.
2. What are the dimensions of T , p , V , n , and R ?
3. List the standard conditions for a gas in the SI and AE systems of units.
4. How do you calculate the density of an ideal gas at S.C.?
5. Can you use the respective specific molar densities (mole/volume) of the gas and the reference gas to calculate the specific gravity of a gas?
6. Does the value of R depend on pressure, temperature, density, or number of moles of a gas?
7. If a gas meets these three conditions, will it behave like an ideal gas?
 - a. The volume occupied by molecules is so small compared to total space that essentially the molecules occupy no space.
 - b. The collisions are so few that it can be said that no energy is lost due to collisions.
 - c. The average distance between the molecules is great enough to neglect the effect of the intermolecular forces.

Problems

1. Calculate the volume in ft^3 of 10 lb mol of an ideal gas at 68°F and 30 psia.
2. A steel cylinder of volume 2 m^3 contains methane gas (CH_4) at 50°C and 250 kPa absolute. How many kilograms of methane are in the cylinder?
3. What is the value of the ideal gas constant R to use if the pressure is to be expressed in atm, the temperature in kelvin, the volume in cubic feet, and the quantity of material in pound moles?
4. Twenty-two kilograms per hour of CH_4 are flowing in a gas pipeline at 30°C and 920 mm Hg. What is the volumetric flow rate of the CH_4 in m^3 per hour?
5. What is the density of a gas that has a molecular weight of 0.123 kg/kg mol at 300 K and 1000 kPa?
6. What is the specific gravity of CH_4 at 70°F and 2 atm compared to air at S.C.?
7. An automobile tire is inflated to a pressure of 35 psig at a temperature of 0°F . Calculate the maximum temperature to which the tire may be heated without the gauge pressure exceeding 50 psia. (Assume that the volume of the tire does not change).

Thought Problems

1. A candle is placed vertically in a soup plate, and the soup plate filled with water. Then the candle is lit. An inverted water glass is carefully placed over the candle. The candle soon goes out, and the water rises inside the glass. It is often said that this shows how much oxygen in the air has been used up. Is this conclusion correct?

2. A scientific supply house markets aerosol-type cans containing compressed helium for filling balloons, doing demonstrations, and the like. On the label there appears the notice: "Because the can contains helium, it quite naturally feels empty. It is actually lighter full than empty." Is this statement correct? If so, why? If not, why not?
3. Some reviewers of books and articles have suggested that the gas constant R in the ideal gas equation be forced to take the value of unity (1). What would this step require as far as using the ideal gas equation?
4. In an article by P. Hickman in *Physics Teacher*, vol. 25, p. 430 (1987) it was suggested that the density of air be determined using marshmallows as follows:
 1. Put the marshmallows in a vacuum so they expand and release trapped air. Repressurize the vessel and compress the marshmallows to a fraction of their original volume.
 2. Weigh the marshmallows on a balance before and after the vacuum treatment. The difference should be the mass of air trapped inside.
 3. Measure their volume before and after the vacuum treatment. The difference should be the volume of the air trapped inside.

Is this a sound way of getting the density of air?

Discussion Problems

1. Three identical glasses are arranged as in Figure DP13.1(P1). Hollow stirrers are also needed. Glasses A and B are completely filled with water (by submerging them jointly in a bucket or sink and joining the mouths before removing), and C is empty. Glasses A and B are carefully placed on a few hollow stirrers as shown in the figure. How can most of the water in glass A be transferred to glass C without ever touching or moving the glasses or their supporting stirrers?

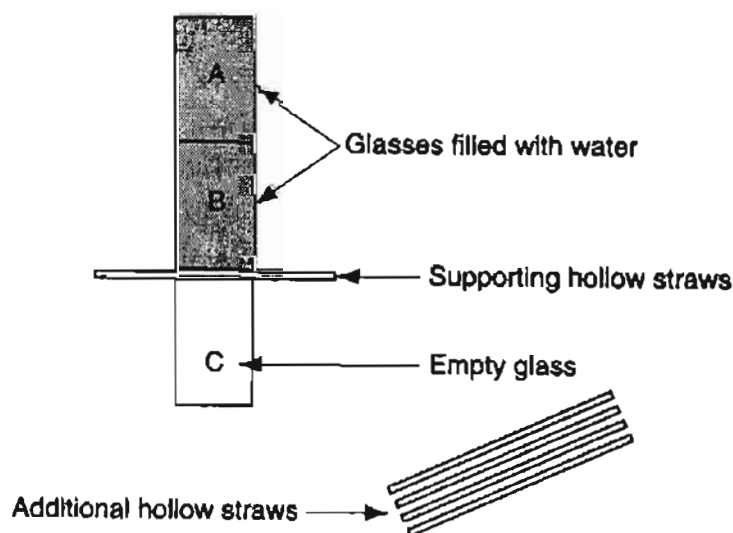


Figure DP13.1P1

2. An employee was cleaning a cylindrical vessel that contained CS_2 in which solid residues had built up on the stirrer. The vessel had been pumped out and blanketed with nitrogen. The manhole cover was removed and the solid residue removed from the stirrer with a scraper rod. The employee went to lunch, leaving the manhole cover off, and after returning to complete the job, started a flash fire with a spark from striking the stirrer with the scraper. What might be some of the causes of the accident?
3. Sea breezes provide welcome relief from the summer heat for residents who live close to the shore. No matter what part of the world—the coast of California, Australia where sea breezes can be very strong, even along the shores of the Great Lakes—the daily pattern in summertime is the same. The sea breeze, a wind blowing from sea to land, begins to develop 3 or 4 hours after sunrise and reaches its peak intensity by mid-afternoon. It may penetrate inland as much as 60 or 70 km. The sea breeze dies out in the evening and 3 or 4 hours after sunset may be replaced by a land breeze, blowing from land to the sea. The land breeze, much weaker than the sea breeze, reaches its peak intensity just before sunrise.

What causes these breezes?

13.2 Ideal Gas Mixtures and Partial Pressure

Frequently, as an engineer, you will want to make calculations for mixtures of gases instead of individual gases. You can use the ideal gas law under the proper assumptions, of course, for a mixture of gases by interpreting p as the total absolute pressure of the mixture, V as the volume occupied by the mixture, n as the total number of moles of all components in the mixture, and T as the absolute temperature of the mixture. As the most obvious example, air is composed of N_2 , O_2 , Ar, CO_2 , Ne, He, and other trace gases, but we can treat air as a single compound in applying the ideal gas law.

When the \$150 million Biosphere project in Arizona began in September 1991, it was billed as a sealed utopian planet in a bottle, where everything would be recycled. Its eight inhabitants lived for two years in the first large self-contained habitat for humans. But slowly the oxygen disappeared from the air—four women and four men in the 3.15 acres of glass domes eventually were breathing air with an oxygen content similar to that found at an altitude of about 13,400 feet. The “thin” air left the group members so fatigued and aching that they sometimes gasped for breath. Finally, the leaders of Biosphere 2 had to pump 21,000 lb of oxygen into the domes to raise the oxygen level from 14.5 to 19.0%. Subsequent investigation of the cause of the decrease in oxygen concluded that microorganisms in the soil that took up oxygen, a factor not accounted for in the design of the biosphere, were the cause of the problem.

Engineers use a fictitious but useful quantity called the **partial pressure** in many of their calculations involving gases. The partial pressure of Dalton, p_i , namely the pressure that would be exerted by a single component in a gaseous mix-

ture if it existed alone in the *same volume* as that occupied by the mixture and at the *same temperature* of the mixture, is defined by

$$p_i V_{\text{total}} = n_i R T_{\text{total}} \quad (13.4)$$

where p_i is the partial pressure of component i in the mixture. If you divide Equation (13.4) by Equation (13.1), you find that

$$\frac{p_i V_{\text{total}}}{p_{\text{total}} V_{\text{total}}} = \frac{n_i R T_{\text{total}}}{n_{\text{total}} R T_{\text{total}}}$$

and

$$p_i = p_{\text{total}} \frac{n_i}{n_{\text{total}}} = p_{\text{total}} y_i \quad (13.5)$$

where y_i is the mole fraction of component i . In air the percent of oxygen is 20.95, hence at the standard conditions of one atmosphere, the partial pressure of oxygen is $p_{\text{O}_2} = 0.2095(1) = 0.2095 \text{ atm}$. Can you show that Dalton's law of the summation of partial pressures is true using Equation (13.5)?

$$p_1 + p_2 + \dots + p_n = p_{\text{total}} \quad (13.6)$$

Although you cannot measure the partial pressure of a gaseous component directly with an instrument, you can calculate the value from Equations (13.5) and/or (13.6). To illustrate the significance of Equation (13.5) and the meaning of partial pressure, suppose that you carried out the following experiment with two nonreacting ideal gases. Examine Figure 13.2. Two tanks each of 1.50 m^3 volume, one containing gas A at 300 kPa and the other gas B at 400 kPa (both gases being at the same temperature of 20°C), are connected to an empty third tank of similar volume. All the gas in tanks A and B is forced into tank C isothermally. Now you have a 1.50-m^3 tank of

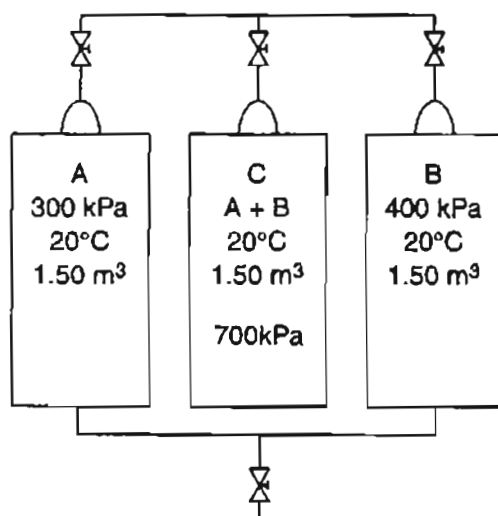


Figure 13.2 Illustration of the meaning of partial pressure of the components of an ideal gas mixture.

A + B at 700 kPa and 20°C for this mixture. You could say that gas A exerts a partial pressure of 300 kPa and gas B exerts a partial pressure of 400 kPa in tank C.

Of course you cannot put a pressure gauge on the tank and check this conclusion because the pressure gauge will read only the total pressure. These partial pressures are hypothetical pressures that the individual gases would exert if they were each put into separate but identical volumes at the same temperature. In tank C the partial pressures of A and B are according to Equation (13.5)

$$p_A = 700 \left(\frac{3}{7} \right) = 300 \text{ kPa}$$

$$p_B = 700 \left(\frac{4}{7} \right) = 400 \text{ kPa}$$

EXAMPLE 13.6 Calculation of the Partial Pressures of the Components in a Gas from a Gas Analysis

Few organisms are able to grow in solution using organic compounds that contain just one carbon atom such as methane or methanol. However, the bacterium *methylococcus capsulatus* can grow under aerobic conditions (in the presence of air) on C-1 carbon compounds. The resulting biomass is a good protein source that can be used directly as feed for domestic animals or fish.

In one process the off-flue gas analyzes 14.0% CO₂, 6.0% O₂, and 80.0% N₂. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution

Use Equation (13.5): $p_i = p_{\text{total}} y_i$

Basis: 1.00 kg (or lb) mol flue gas

Component	kg (or lb) mol	p (mm Hg)
CO ₂	0.140	107.1
O ₂	0.060	45.9
N ₂	0.800	612.0
Total	1.000	765.0

On the basis of 1.00 mole of flue gas, the mole fraction y of each component, when multiplied by the total pressure, gives the partial pressure of that component. If you find that the temperature measurement of the flue gas was actually 437°F but the pressure measurement was correct, would the partial pressures change? Hint: Is the temperature involved in Equation 13.5?

SELF-ASSESSMENT TEST**Questions**

1. A partial pressure of oxygen in the lungs of 100 mm Hg is adequate to maintain oxygen saturation of the blood in a human. Is this value higher or lower than the partial pressure of oxygen in the air at sea level?
2. An exposure to a partial pressure of N_2 of 1200 mm Hg in air has been found by experience not to cause the symptoms of N_2 intoxication to appear. Will a diver at 60 meters be affected by the N_2 in the air being breathed?
3. If 1.72 m^3 of a gas mixture of 30% CO_2 and 70% N_2 at 20°C and 105 kPa in a balloon is heated to 70°C , will the partial pressure of the CO_2 in the balloon increase or decrease?
4. If you add neon isothermally to helium in a fixed volume vessel, will the partial pressure of the helium change?

Problems

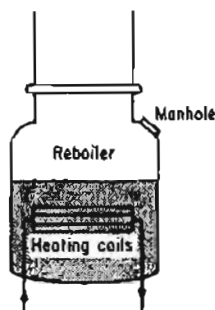
1. A gas has the following composition at 120°F and 13.8 psia.

Component	Mol %
N_2	2
CH_4	79
C_2H_6	19

- a. What is the partial pressure of each component?
 - b. What is the volume fraction of each component?
2. a. If the C_2H_6 were removed from the gas in Problem 1, what would be the subsequent pressure in the vessel?
 - b. What would be the subsequent partial pressure of the N_2 ?

Discussion Problem

1. A distillation column reboiler in a room, as shown in Figure DP13.2P1, had been cleaned, but the manhole cover was not securely fastened on startup again. As a result, benzene vapor escaped from the manhole and one operator died by asphyxiation. How could this accident have occurred?

**Figure DP13.2P1**

13.3 Material Balances Involving Ideal Gases

Now that you have had a chance to practice applying the ideal gas law to simple problems, let's apply the ideal gas law in material balances. The only difference between the subject matter of Chapters 6 through 12 and this chapter is that here the amount of material can be specified in terms of p , V , and T rather than solely mass or moles. For example, the basis for a problem, or the quantity to be solved for, might be a volume of gas at a given temperature and pressure rather than a mass of gas. The next two examples illustrate material balances for problems similar to those you have encountered before, but now involve gases.

EXAMPLE 13.7 Material Balances for a Process Involving Combustion

To evaluate the use of renewable resources, an experiment was carried out to pyrolyze rice hulls. The product gas analyzed 6.4 % CO_2 , 0.1% O_2 , 39% CO , 51.8% H_2 , 0.6% CH_4 , and 2.1% N_2 . It entered the combustion chamber at 90°F and a pressure of 35.0 in. Hg, and was burned with 40% excess air (dry), which was at 70°F and an atmospheric pressure of 29.4 in. Hg; 10% of the CO remained unburned. How many cubic feet of air were supplied per cubic foot of entering gas? How many cubic feet of product gas were produced per cubic foot of entering gas if the exit gas was at 29.4 in. Hg and 400°F ?

Solution

This is an open, steady-state system with reaction. The system is the combustion chamber.

Steps 1, 2, 3, and 4

Figure E13.7 illustrates the process and notation. With 40% excess air, certainly all of the CO , H_2 , and CH_4 should burn to CO_2 and H_2O ; apparently, for some unknown reason, not all of the CO burns to CO_2 . The components of the product gas are shown in the figure.

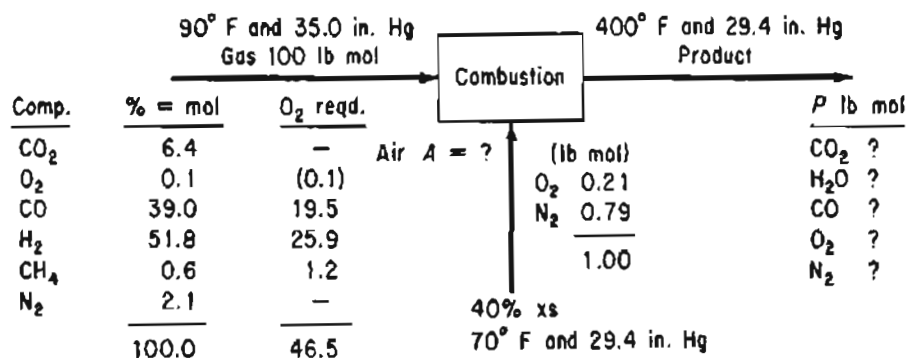


Figure E13.7

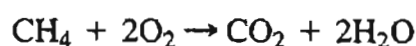
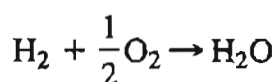
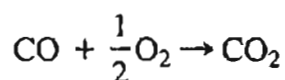
Step 5

You could take 1 ft³ at 90°F and 35.0 in. Hg as the basis, and convert the volume to moles, but it is just as easy to take 100 lb mol as a basis because then % = lb mol. At the end of the problem you can convert lb mol to ft³.

Basis: 100 lb mol pyrolysis gas

Step 4 (continued)

The entering air can be calculated from the specified 40% excess air; the reactions for complete combustion are



The moles of oxygen required are listed in Figure E13.7. The excess oxygen is

$$\text{Excess O}_2: 0.4(46.5) = 18.6$$

$$\text{Total O}_2 = 46.5 + 18.6 = 65.1$$

$$\text{N}_2 \text{ in is } 65.1 \left(\frac{79}{21} \right) = 244.9$$

Total moles of air in are $244.9 + 65.1 = 310.0$ lb mol.

Steps 6 and 7

Let's make a reduced degree-of-freedom analysis. Five unknowns exist, the five products. You can make four element balances and you know the fraction of the entering CO that exists in *P* so that you can calculate $n_{\text{CO}}^{\text{out}} = 0.10(39) = 3.9$. Hence the problem has zero degrees of freedom.

Steps 8 and 9

Make element balances in moles to calculate the values of the unknown quantities, and substitute the value of 3.9 for the number of moles of CO exiting.

	<i>In</i>		<i>Out</i>
2N:	2.1 + 244.9	=	n_{N_2}
C:	6.4 + 39.0 + 0.6	=	$n_{\text{CO}_2} + 3.9$
2H:	51.8 + 0.6(2)	=	$n_{\text{H}_2\text{O}}$
2O:	6.4 + 0.1 + 0.5(39) + 65.1	=	$n_{\text{O}_2} + n_{\text{CO}_2} + 0.5(n_{\text{H}_2\text{O}} + n_{\text{CO}})$

The solution of these equations is

$$n_{\text{N}_2} = 247 \quad n_{\text{CO}_2} = 42.1 \quad n_{\text{H}_2\text{O}} = 53.0 \quad n_{\text{O}_2} = 20.55$$

and $n_{\text{CO}} = 3.9$

The total moles exiting sum to 366.6 lb mol.

If you prefer to make species balances, let n_i^{out} be the moles of species i exiting the process. The degree-of-freedom analysis is (the basis is 100 g mol entering):

Unknowns (11): $n_{\text{CO}_2}^{\text{out}}, n_{\text{O}_2}^{\text{out}}, n_{\text{CO}}^{\text{out}}, n_{\text{H}_2}^{\text{out}}, n_{\text{CH}_4}^{\text{out}}, n_{\text{H}_2\text{O}}^{\text{out}}, n_{\text{N}_2}^{\text{out}}, \xi_1, \xi_2, \xi_3, P$

Equations and specifications (11).

Material balances

$$\text{CO}_2: n_{\text{CO}_2}^{\text{out}} - 39 = -\xi_1$$

$$\text{O}_2: n_{\text{O}_2}^{\text{out}} - 1 - 65.1 = -0.5\xi_1 - 0.5\xi_2 - 2\xi_3$$

$$\text{CO}: n_{\text{CO}}^{\text{out}} - 6.4 = \xi_1 + \xi_2$$

$$\text{H}_2: n_{\text{H}_2}^{\text{out}} - 51.8 = \xi_2$$

$$\text{CH}_4: n_{\text{CH}_4}^{\text{out}} - 0.6 = -\xi_3$$

$$\text{H}_2\text{O}: n_{\text{H}_2\text{O}}^{\text{out}} - 0 = \xi_1 + 2\xi_3$$

$$\text{N}_2: n_{\text{N}_2}^{\text{out}} - 2.1 - 244.9 = 0 \text{ (no reaction)}$$

Specifications:

$$n_{\text{H}_2}^{\text{out}} = 0$$

$$n_{\text{CH}_4}^{\text{out}} = 0$$

$$n_{\text{CO}}^{\text{out}} = 0.1(39) = 3.9$$

Implicit relations:

$$\sum n_i^{\text{out}} = P$$

The degrees of freedom are zero. Solution of these equations gives the same results as the element balances, as expected.

Finally, you can convert the lb mol of air and products that were calculated on the basis of 100 lb mol of pyrolysis gas to the volumes of gases at the states requested:

$$T_{\text{gas}} = 90 + 460 = 550^\circ\text{R}$$

$$T_{\text{air}} = 70 + 460 = 530^\circ\text{R}$$

$$T_{\text{product}} = 400 + 460 = 860^\circ\text{R}$$

$$\text{ft}^3 \text{ of gas: } \frac{100 \text{ lb mol entering gas}}{1 \text{ lb mol}} \left| \frac{359 \text{ ft}^3 \text{ at SC}}{1 \text{ lb mol}} \right| \frac{550^\circ\text{R}}{492^\circ\text{R}} \left| \frac{29.92 \text{ in. Hg}}{35.0 \text{ in. Hg}} \right| = 343 \times 10^2$$

$$\text{ft}^3 \text{ of air: } \frac{310 \text{ lb mol air}}{1 \text{ lb mol}} \left| \frac{359 \text{ ft}^3 \text{ at SC}}{1 \text{ lb mol}} \right| \frac{530^\circ\text{R}}{492^\circ\text{R}} \left| \frac{29.92 \text{ in. Hg}}{29.4 \text{ in. Hg}} \right| = 1220 \times 10^2$$

$$\text{ft}^3 \text{ of product: } \frac{366.6 \text{ lb mol } P}{1 \text{ lb mol}} \left| \frac{359 \text{ ft}^3 \text{ at SC}}{1 \text{ lb mol}} \right| \frac{860^\circ\text{R}}{492^\circ\text{R}} \left| \frac{29.92 \text{ in. Hg}}{35.0 \text{ in. Hg}} \right| = 2255 \times 10^2$$

The answers to the questions are

$$\frac{1220 \times 10^2}{343 \times 10^2} = 3.56 \frac{\text{ft}^3 \text{ air at } 530^\circ\text{R and } 29.4 \text{ in. Hg}}{\text{ft}^3 \text{ gas at } 550^\circ\text{R and } 35.0 \text{ in. Hg}}$$

$$\frac{2255 \times 10^2}{343 \times 10^2} = 6.57 \frac{\text{ft}^3 \text{ product at } 860^\circ\text{R and } 29.4 \text{ in. Hg}}{\text{ft}^3 \text{ gas at } 550^\circ\text{R and } 35.0 \text{ in. Hg}}$$

EXAMPLE 13.8 Material Balance without Reaction

Gas at 15°C and 105 kPa is flowing through an irregular duct. To determine the rate of flow of the gas, CO_2 from a tank is passed into the gas stream. The gas analyzes 1.2% CO_2 by volume before and 3.4% CO_2 by volume after the addition. As the CO_2 that was injected left the tank, it was passed through a rotameter, and found to flow at the rate of $0.0917 \text{ m}^3/\text{min}$ at 7°C and 131 kPa . What was the rate of flow of the entering gas in the duct in cubic meters per minute?

Solution

This is an open, steady-state system without reaction. The system is the duct. Figure E13.8 is a sketch of the process.

Steps 1, 2, 3, and 4

The data are presented in Figure E13.8.

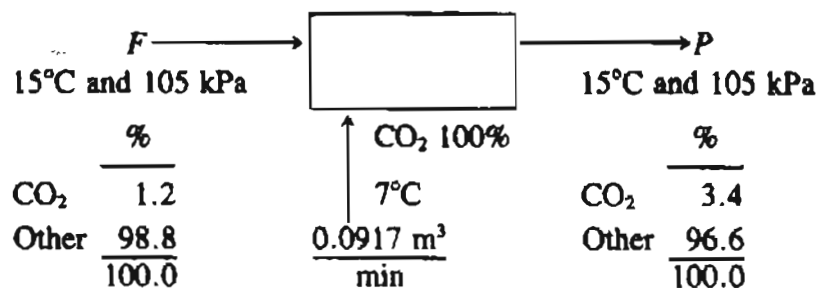


Figure E13.8

Both F and P are at the same temperature and pressure.

Step 5

Should you take as a basis 1 min = 0.0917 m³ of CO₂ at 7°C and 131 kPa? The gas analysis is in volume percent, which is the same as mole percent. We could convert the 0.0917 m³ to moles and solve the problem in terms of moles, but there is no need to do so because we just as easily convert the known flow rate of the addition of CO₂ to a volume at 15°C and 105 kPa, and solve the problem using m³ for each stream since all the streams are at the same conditions. We could similarly convert all of the data to 7°C and 131 kPa, but more calculations would be required to get the answer than for 15°C and 105 kPa. Thus, we start with the basis of

$$\frac{0.0917 \text{ m}^3}{273 + 7} \left| \frac{273 + 15}{105} \right| \frac{131}{105} = 0.1177 \text{ m}^3 \text{ at } 15^\circ\text{C and } 105 \text{ kPa}$$

Steps 6 and 7

We do not know F and P , but can make two independent component balances, CO₂ and "other," hence the problem has zero degrees of freedom.

Steps 7, 8, and 9

$$\text{"Other" balance (in m}^3 \text{ at } 15^\circ\text{C and } 105 \text{ kPa): } F(0.988) = P(0.966) \quad (\text{a})$$

$$\text{CO}_2 \text{ balance (in m}^3 \text{ at } 15^\circ\text{C and } 105 \text{ kPa): } F(0.012) + 0.1177 = P(0.034) \quad (\text{b})$$

$$\text{Total balance (in m}^3 \text{ at } 15^\circ\text{C and } 105 \text{ kPa): } F + 0.1177 = P \quad (\text{c})$$

Note that the "other" is a tie component. Select Equations (a) and (c) to solve. The solution of Equations (a) and (c) gives

$$F = 5.17 \text{ m}^3/\text{min at } 15^\circ\text{C and } 105 \text{ kPa}$$

Step 10 (Check)

Use the redundant equation:

$$\text{By Equation (b): } 5.17(0.012) + 0.1177 = 0.180 \underline{\underline{2}}$$

$5.17(0.988/0.966)(0.034) = 0.180$ The equation checks out to a satisfactory degree of precision.

SELF-ASSESSMENT TEST

Questions

1. How does the introduction of ideal gases affect the principles involved in making material balances?

2. Does including the ideal gas law together with material balances add an additional equation to the analysis of the degrees of freedom?

Problems

1. A furnace is fired with 1000 ft³ per hour at 60°F and 1 atm of a natural gas having the following volumetric analysis: CH₄: 80%, C₂H₆: 16%, O₂: 2%, CO₂: 1%, and N₂: 1%. The exit flue gas temperature is 800°F and the pressure is 760 mm Hg absolute; 15% excess air is used and combustion is complete. Calculate the (a) volume of CO₂ produced per hour; (b) volume of H₂O vapor produced per hour; (c) volume of N₂ produced per hour; and (d) total volume of flue gas produced per hour.
2. A flue gas contains 60% N₂ and is mixed with air to cool it. If the resulting mixture flows at a rate of 250,000 ft³ /hr and contains 70% N₂, what is the flow rate of the flue gas? State all your assumptions concerning the temperatures and pressures of the gas streams.
3. Two tanks containing N₂ at the following conditions sit next to each other

	Tank A	Tank B
Volume (m ³)	1	5
Temperature (°C)	25	40
Pressure (kPa)	300	?
Amount of gas (g mol)	?	?

After the two tanks are connected and reach equilibrium, the conditions in the combined tanks are 700 kPa and 35°C. What was the pressure in Tank B?

Thought Problems

1. In a test of the flow of gases through a pipe, pure hydrogen was found to flow at a volumetric flow rate 22 times that of carbon dioxide. When the hydrogen was diluted with carbon dioxide entering the pipe midway from the ends, the exit flow rate was less than that of pure hydrogen. Explain the observed differences.
2. A pair of identical balloons are inflated with air to the same pressure, and tied to a stick that is held in the center by a string. The balloons are each the same distance from the center of the stick so that the stick remains horizontal to the ground. When the lefthand balloon is carefully punctured, will the stick rotate down from the left, up from the left, or remain horizontal?

Discussion Problem

1. In a demonstration, a 30 cm diameter balloon was filled to two-thirds of its maximum pressure with SF₆, a gas. Students measured the balloon's diameter for 10 days, at which time the balloon burst. No one ever touched it. Explain how this could happen. (Note: The balloon was not defective.)

Looking Back

We reviewed the ideal gas law as applied to pure components and gas mixtures, and explained about density and specific gravity for gases. In making balances, process measurements are frequently made as volumetric flows rather than molar or mass flows, and the molar flows can be calculated from the volumetric flows as well as the reverse.

GLOSSARY OF NEW WORDS

- Dalton's Law** The summation of each of the partial pressures of the components in a system equals the total pressure. The other related law (of partial pressures) is that the total pressure times the mole fraction of a component in a system is the partial pressure of the component.
- Density of gas** Mass per unit volume expressed in kg/m^3 , lb/ft^3 , g/L , or equivalent units.
- Ideal gas constant** The constant in the ideal gas law (and other equations) denoted by the symbol R .
- Ideal gas law** Equation relating p , V , n , and T that applies to many gases at low density (high temperature and/or low pressure).
- Partial pressure** The pressure that would be exerted by a single component in a gaseous mixture if it existed alone in the same volume as occupied by the mixture and at the temperature of the mixture.
- Specific gravity** Ratio of the density of a gas at a temperature and pressure to the density of a reference gas at some temperature and pressure.
- Standard conditions (S.C.)** Arbitrarily specified standard states of temperature and pressure established for gases by custom.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent.

Black, W.Z., and J.G. Hartley. *Thermodynamics*, Harper & Row, New York (1985).

Howell, J.R., and R.O. Buckius. *Fundamentals of Engineering Thermodynamics*, McGraw-Hill, New York (1987).

- Masavetas, K.A. "The Mere Concept of an Ideal Gas," *Math. Comput. Modelling*, **12**, 651–657 (1989).
- Van Wylen, G.J., and R.E. Sonntag. *Fundamentals of Classical Thermodynamics*, 3rd ed., John Wiley, New York (1985).
- Wark, K. *Thermodynamics*, 5th ed., McGraw-Hill, New York (1988).

Web Sites

<http://antoine.frostburg.edu/chem/senese/101/matter/resources.shtml>
<http://chemistry.ohiostate.edu/betba/realgaslaw/fr22.html>
<http://eng.sdsu.edu/testcenter/Test/solv...t/idealgasidealgas/idealgasidealgas.html>
<http://mccoy.lib.siu.edu/projects/chem200/audiolinks.html>
<http://voyager5.sdsu.edu/testcenter/home.html>

PROBLEMS

- *13.1 How many pounds of H_2O are in 100 ft^3 of vapor at 15.5 mm Hg and 23°C ?
- *13.2 One liter of a gas is under a pressure of 780 mm Hg. What will be its volume at standard pressure, the temperature remaining constant?
- *13.3 A gas occupying a volume of 1 m^3 under standard pressure is expanded to 1.200 m^3 , the temperature remaining constant. What is the new pressure?
- *13.4 Determine the mass specific volume and molal specific volume for air at 78°F and 14.7 psia.
- *13.5 An oxygen cylinder used as standby source of oxygen contains 1.000 ft^3 of O_2 at 70°F and 200 psig. What will be the volume of this O_2 in a dry-gas holder at 90°F and 4.00 in. H_2O above atmospheric? The barometer reads 29.92 in. Hg.
- *13.6 You have 10 lb of CO_2 in a 20-ft^3 fire extinguisher tank at 30°C . Assuming that the ideal gas law holds, what will the pressure gauge on the tank read in a test to see if the extinguisher is full?
- *13.7 Divers work as far as 500 ft below the water surface. Assume that the water temperature is 45°F . What is the molar specific volume ($\text{ft}^3/\text{lb mol}$) for an ideal gas under these conditions?
- *13.8 A 25-L glass vessel is to contain 1.1 g moles of nitrogen. The vessel can withstand a pressure of only 20 kPa above atmospheric pressure (taking into account a suitable safety factor). What is the maximum temperature to which the N_2 can be raised in the vessel?
- *13.9 An oxygen cylinder used as a standby source of oxygen contains O_2 at 70°F . To calibrate the gauge on the O_2 cylinder which has volume of 1.01 ft^3 , all of the oxygen, initially at 70°F , is released into an evacuated tank of known volume (15.0 ft^3). At

equilibrium, the gas pressure was measured as 4 in. H_2O gauge and the gas temperature in both cylinders was $75^\circ F$. See Fig. P13.9. The barometer read 29.99 in. Hg.

What did the pressure gauge on the oxygen tank initially read in psig if it was a Bourdon gauge?

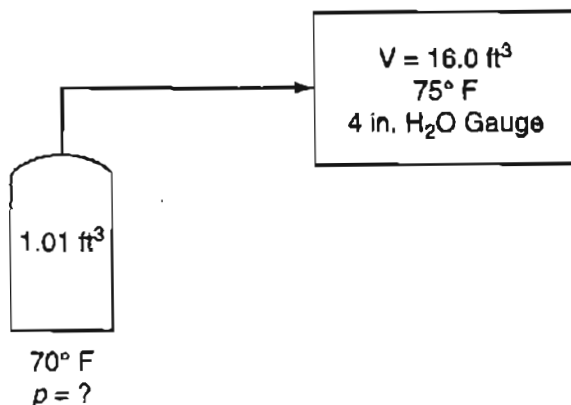


Figure P13.9

- **13.10** The U-tube manometer depicted in Figure P13.10 has a left leg 20 inches high and a right leg 40 inches high. The manometer initially contains mercury to a depth of 12 inches in each leg. Then the left leg is closed with a cork, and mercury is poured in the right leg until the mercury in the left (closed) leg reaches a height of 14 inches. How deep is the mercury in the right leg from the bottom of the manometer?

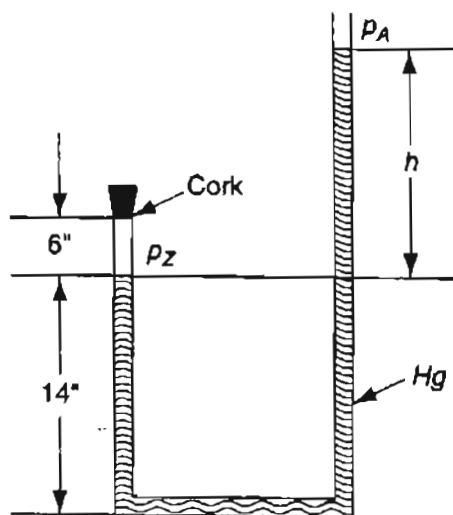


Figure P13.10

- ***13.11** One of the experiments in the fuel-testing laboratory has been giving some trouble because a particular barometer gives erroneous readings owing to the presence of a small amount of air above the mercury column. At a true atmospheric pressure of 755 mm Hg the barometer reads 748 mm Hg, and at a true 740 mm Hg the reading is 736 mm Hg. What will the barometer read when the actual pressure is 760 mm Hg?

- *13.12 An average person's lungs contain about 5 L of gas under normal conditions. If a diver makes a free dive (no breathing apparatus), the volume of the lungs is compressed when the pressure equalizes throughout the body. If compression occurs below 1L, irreversible lung damage will occur. Calculate the maximum safe depth for a free dive in sea water (assume the density is the same as fresh water).
- *13.13 An automobile tire when cold (at 75°F) reads 30 psig on a tire gage. After driving on the freeway, the temperature in the tire becomes 140°F. Will the pressure in the tire exceed the pressure limit of 35 psi the manufacturer stamps on the tire?
- *13.14 You are making measurements on an air conditioning duct to test its load capacity. The warm air flowing through the circular duct has a density of 0.0796 pounds per cubic foot. Careful measurements of the velocity of the air in the duct disclose that the average air velocity is 11.3 feet per second. The inside radius of the duct is 18.0 inches. What is (a) the volumetric flow rate of the air in ft³/hr, and (b) what is the mass flow rate of the air in lb/day?
- *13.15 Flue gas at a temperature of 1800°F is introduced to a scrubber through a pipe which has an inside diameter of 4.0 ft. The inlet velocity to and the outlet velocity from the scrubber are 25 ft/s and 20 ft/s, respectively. The scrubber cools the flue gas to 550°F. Determine the duct size required at the outlet of the unit.
- *13.16 Calculate the number of cubic meters of hydrogen sulphide, measured at a temperature of 30°C and a pressure of 15.71 cm of Hg, which may be produced from 10 kg of iron sulphide (FeS).
- *13.17 One pound mole of flue gas has the following composition. Treat it as an ideal gas.

CO₂ (11.2%), CO (1.2%), SO₂ (1.2%), O₂ (5.3%), N₂ (81.0%), H₂O (0.1%)

How many ft³ will the gas occupy at 100°F and 1.54 atm?

- *13.18 Monitoring of hexachlorobenzene (HCB) in a flue gas from an incinerator burning 500 lb/hr of hazardous wastes is to be conducted. Assume that all of the HCB is removed from a sample of the flue gas and concentrated in 25 mL of solvent. The analytical detection limit for HCB is 10 micrograms per milliliter in the solvent. Determine the minimum volume of flue gas that has to be sampled to detect the existence of HCB in the flue gas. Also, calculate the time needed to collect a gas sample if you can collect 1.0 L per minute. The flue gas flow rate is 427,000 ft³/hr measured at standard conditions.
- *13.19 Ventilation is an extremely important method of reducing the level of toxic airborne contaminants in the workplace. Since it is impossible to eliminate absolutely all leakage from a process into the workplace, some method is always needed to remove toxic materials from the air in closed rooms when such materials are present in the process streams. The Occupational Safety and Health Administration (OSHA) has set the permissible exposure limit (PEL) of vinyl chloride (VC, MW = 78) at 1.0 ppm as a maximum time-weighted average (TWA) for an eight-hour workday, because VC is believed to be a human carcinogen. If VC escaped into the air, its concentration must be maintained at or below the PEL. If dilution ventilation were to be used, you can estimate the required air flow rate by assuming complete mixing in the workplace air,

and then assume that the volume of air flow through the room will carry VC out with it at the concentration of 1.0 ppm.

If a process loses 10 g/min of VC into the room air, what volumetric flow rate of air will be necessary to maintain the PEL of 1.0 ppm by dilution ventilation? (In practice we must also correct for the fact that complete mixing will not be realized in a room so that you must multiply the calculated air flow rate by a safety factor, say a factor of 10.)

If the safety analysis or economics of ventilation do not demonstrate a safe concentration of VC exists, the process might have to be moved into a hood so that no VC enters the room. If the process is carried out in a hood with an opening of 30 in. wide by 25 in. high, and the "face velocity" (average air velocity through the hood opening) is 100 ft/s, what is the volumetric air flow rate at SC? Which method of treating the pollution problem seems to be the best to you? Explain why dilution ventilation is not recommended for maintaining air quality. What might be a problem with the use of a hood? The problem is adapted with permission from the publication *Safety, Health, and Loss Prevention in Chemical Processes* published by The American Institute of Chemical Engineers, New York (1990).

- *13.20** Ventilation is an extremely important method of reducing the level of toxic airborne contaminants in the workplace. Trichloroethylene (TCE) is an excellent solvent for a number of applications, and is especially useful in degreasing. Unfortunately, TCE can lead to a number of harmful health effects, and ventilation is essential. TCE has been shown to be carcinogenic in animal tests. (Carcinogenic means that exposure to the agent might increase the likelihood of the subject getting cancer at some time in the future.) It is also an irritant to the eyes and respiratory tract. Acute exposure causes depression of the central nervous system, producing symptoms of dizziness, tremors, and irregular heartbeat, plus others.

Since the molecular weight of TCE is approximately 131.5, it is much more dense than air. As a first thought, you would not expect to find a high concentration of this material above an open tank because you might assume that the vapor would sink to the floor. If this were so, then we would place the inlet of a local exhaust hood for such a tank near the floor. However, toxic concentrations of many materials are not much more dense than the air itself, so where there can be mixing with the air we may not assume that all the vapors will go to the floor. For the case of trichloroethylene OSHA has established a time-weighted average 8 hr permissible exposure limit (PEL) of 100 ppm. What is the fraction increase in the density of a mixture of TCE in air over that of air if the TCE is at a concentration of 100 ppm and at 25°C? This problem has been adapted from *Safety, Health, and Loss Prevention in Chemical Processes*, New York: American Institute of Chemical Engineers, (1990): 3.

- *13.21** Benzene can cause chronic adverse blood effects such as anemia and possibly leukemia with chronic exposure. Benzene has a PEL (permissible exposure limit) for an 8-hr exposure of 1.0 ppm. If liquid benzene is evaporating into the air at a rate of 2.5 cm³ of liquid/min, what must the ventilation rate be in volume per minute to keep the concentration below the PEL? The ambient temperature is 68°F and the pressure is 740 mm Hg. This problem has been adapted from *Safety, Health, and Loss Preven-*

tion in *Chemical Processes*, New York: American Institute of Chemical Engineers, (1990): 6.

- *13.22 A recent newspaper report states: "Home meters for fuel gas measure the volume of gas usage based on a standard temperature, usually 60 degrees. But gas contracts when it's cold and expands when warm. East Ohio Gas Co. figures that in chilly Cleveland, the homeowner with an outdoor meter gets more gas than the meter says he does, so that's built into the company's gas rates. The guy who loses is the one with an indoor meter: If his home stays at 60 degrees or over, he'll pay for more gas than he gets. (Several companies make temperature-compensating meters, but they cost more and aren't widely used. Not surprisingly, they are sold mainly to utilities in the North.)" Suppose that the outside temperature drops from 60°F to 10°F. What is the percentage increase in the mass of the gas passed by a noncompensated outdoor meter that operates at constant pressure? Assume that the gas is CH_4 .

- *13.23 Soft ice cream is a commercial/ice cream mixture whipped usually with CO_2 (as the O_2 in the air causes deterioration.) You are working in the Pig-in-a-Poke Drive-In and need to make a machine full (4 gal) of soft ice cream. The unwhipped mix has a sp. gr. of 0.95 and the local ordinance forbids you to make ice cream of less than sp. gr. of 0.85. Your CO_2 tank is a No. 1 cylinder (9 in. diameter by 52 in. high) of commercial grade (99.5% min. CO_2) carbon dioxide. In examining the pressure gauge you note it reads 68 psig. Do you have to order another cylinder of CO_2 ? Be sure to specifically state all the assumptions you make for this problem.

Additional Data:

Atmospheric pressure is 752 mm Hg

sp. gr. cream = 0.84

sp. gr. milk = 0.92

Butterfat content of soft ice cream is less than 14%

- *13.24 From the known standard conditions, calculate the value of the gas law constant R in the following sets of units:

(a) $\text{cal}/(\text{g mol})(\text{K})$

(d) $\text{J}/(\text{g mol})(\text{K})$

(b) $\text{Btu}/(\text{lb mol})(^\circ\text{R})$

(e) $(\text{cm}^3)(\text{atm})/(\text{g mol})(\text{K})$

(c) $(\text{psia})(\text{ft}^3)/(\text{lb mol})(^\circ\text{R})$

(f) $(\text{ft}^3)(\text{atm})/(\text{lb mol})(^\circ\text{R})$

- *13.25 What is the density of O_2 at 100°F and 740 mm Hg in (a) lb/ft^3 and (b) g/L ?

- *13.26 What is the density of propane gas (C_3H_8) in kg per cubic meter at 200 kPa and 40°C? What is the specific gravity of propane?

- *13.27 What is the specific gravity of propane gas (C_3H_8) at 100°F and 800 mm Hg relative to air at 60°F and 760 mm Hg?

- *13.28 What is the mass of 1 m^3 of H_2 at 5°C and 110 kPa? What is the specific gravity of this H_2 compared to air at 5°C and 110 kPa?

- *13.29 A natural gas has the following composition:

CH_4 (methane) 87%

C_2H_6 (ethane) 12%

C_3H_8 (propane) 1%

- (a) What is the composition in weight percent?
 (b) What is the composition in volume percent?
 (c) How many m^3 will be occupied by 80.0 kg of the gas at 9°C and 600 kPa?
 (d) What is the density of the gas in kg/m^3 at SC?
 (e) What is the specific gravity of this gas at 9°C and 600 kPa referred to air at SC?
- *13.30** A mixture of bromine vapor in air contains 1% bromine by volume.
 (a) What weight percent bromine is present?
 (b) What is the average molecular weight of the mixture?
 (c) What is its specific gravity?
 (d) What is its specific gravity compared to bromine?
 (e) What is its specific gravity at 100°F and 100 psig compared to air at 60°F and 30 in. Hg?
- *13.31** A gas used to extinguish fires is composed of 80% CO_2 and 20% N_2 . It is stored in a 2 m^3 tank at 200 kPa and 25°C . What is the partial pressure of the CO_2 in the tank in kPa?
- *13.32** A natural gas has the following composition by volume:
- | | |
|---------------|------------|
| CH_4 | 94.1% |
| N_2 | 3.0 |
| H_2 | 1.9 |
| O_2 | <u>1.0</u> |
| | 100.0% |
- This gas is piped from the well at a temperature of 20°C and a pressure of 30 psig. It may be assumed that the ideal gas law is applicable. Calculate the partial pressure of the oxygen.
- *13.33** A liter of oxygen at 760 mm Hg is forced into a vessel containing a liter of nitrogen at 760 mm Hg. What will be the resulting pressure? What assumptions are necessary for your answer?
- *13.34** The contents of a gas cylinder are found to contain 20 percent CO_2 , 60 percent O_2 , and 20 percent N_2 at a pressure of 740 mm Hg and at 20°C . What are the partial pressures of each of the components? If the temperature is raised to 40°C , will the partial pressures change? If so, what will they be?
- *13.35** Methane is completely burned with 20% excess air, with 30% of the carbon going to CO. What is the partial pressure of the CO in the stack gas if the barometer reads 740 mm Hg, the temperature of the stack gas is 300°F , and the gas leaves the stack at 250 ft above the ground level?
- *13.36** Answer the following questions true or false:
- The volume of an ideal-gas mixture is equal to the sum of the volumes of each individual gas in the mixture.
 - The temperature of an ideal-gas mixture is equal to the sum of the temperatures of each individual gas in the mixture.
 - The pressure of an ideal-gas mixture is equal to the sum of the partial pressures of each individual gas in the mixture.

- *13.37** A 0.5-m^3 rigid tank containing hydrogen at 20°C and 600 kPa is connected by a valve to another 0.5-m^3 rigid tank that holds hydrogen at 30°C and 150 kPa . Now the valve is opened and the system is allowed to reach thermal equilibrium with the surroundings, which are at 15°C . Determine the final pressure in the tank.
- **13.38** A 400 ft^3 tank of compressed H_2 is at a pressure of 55 psig . It is connected to a smaller tank with a valve and short line. The small tank has a volume of 50 ft^3 and contains H_2 at 1 atmosphere absolute and the same temperature. If the interconnecting valve is opened and no temperature change occurs, what is the final pressure in the system?
- **13.39** A tank of N_2 has a volume of 100 ft^3 and an initial temperature of 80°F . One pound of N_2 is removed from the tank, and the pressure drops to 100 psig while the temperature of the gas in the tank drops to 60°F . Assuming N_2 acts as an ideal gas, calculate the initial pressure reading on the pressure gage.
- *13.40** Measurement of flue gas flow rates is difficult by traditional techniques for various reasons. Tracer gas flow measurements using sulfur hexafluoride (SF_6) have proved to be more accurate. The accompanying figure shows the stack arrangement and the injection and sampling points for the SF_6 . Here is the data for one experiment:

Volume of SF_6 injected (converted to SC): $28.8\text{ m}^3/\text{min}$

Concentration of SF_6 at the flue gas sample point: 4.15 ppm

Relative humidity correction: none

Calculate the volume of the exit flue gas per minute.

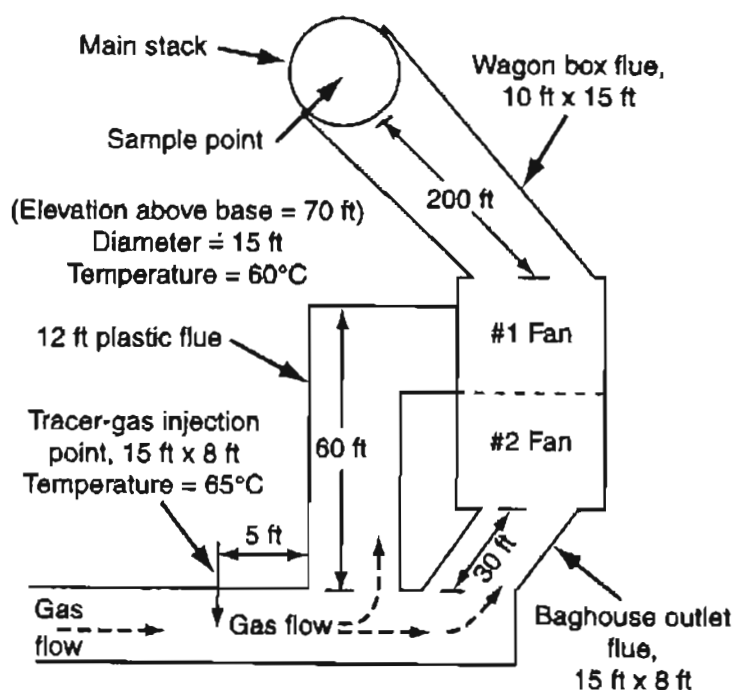
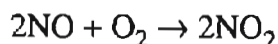


Figure P13.40

- *13.41 An ideal gas at 60°F and 31.2 in. Hg (absolute) is flowing through an irregular duct. To determine the flow rate of the gas, CO₂ is passed into the gas stream. The gas analyzes 1.2 mole % CO₂ before and 3.4 mole % after addition. The CO₂ tank is placed on a scale and found to lose 15 lb in 30 minutes. What is the flow rate of the entering gas in cubic feet per minute?
- **13.42 One important source of emissions from gasoline-powered automobile engines that causes smog is the nitrogen oxides NO and NO₂. They are formed whether combustion is complete or not as follows. At the high temperatures that occur in an internal combustion engine during the burning process, oxygen and nitrogen combine to form nitric oxide (NO). The higher the peak temperatures and the more oxygen available, the more NO is formed. There is insufficient time for the NO to decompose back to O₂ and N₂ because the burned gases cool too rapidly during the expansion and exhaust cycles in the engine. Although both NO and nitrogen dioxide (NO₂) are significant air pollutants (together termed NO_x), the NO₂ is formed in the atmosphere as NO is oxidized.

Suppose that you collect a sample of a NO-NO₂ mixture (after having removed the other combustion gas products including N₂, O₂ and H₂O by various separations procedures) in a 100-cm³ standard cell at 30°C. Certainly some of the NO will have been oxidized to NO₂



during the collection, storage, and processing of the combustion gases, so that measurement of NO alone will be misleading. If the standard cell contains 0.291 g of NO₂ plus NO and the pressure measured in the cell is 170 kPa, what percent of the NO + NO₂ is in the form of NO?

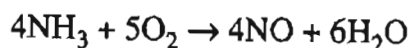
- *13.43 In the manufacture of dry ice, a fuel is burned to a flue gas which contains 16.2 percent CO₂, 4.8 percent O₂, and the remainder N₂. This flue gas passes through a heat exchanger and then goes to an absorber. The data show that the analysis of the flue gas entering the absorber is 13.1 percent CO₂ with the remainder O₂ and N₂. Apparently something has happened. To check your initial assumption that an air leak has developed in the heat exchanger, you collect the following data on a dry basis on the heat exchanger:

Entering flue gas in a 2-min period 47,800 ft³ at 600°F and 740 mm of Hg

Exit flue gas in a 2-min period 30,000 ft³ at 60°F and 720 mm of Hg

Was your assumption about an air leak a good one, or was perhaps the analysis of the gas in error? Or both?

- **13.44 Ammonia at 100°C and 150 kPa is burned with 20% excess O₂



The reaction is 80% complete. The NO is separated from the NH₃ and water, and the NH₃ is recycled as shown in Figure P13.44.

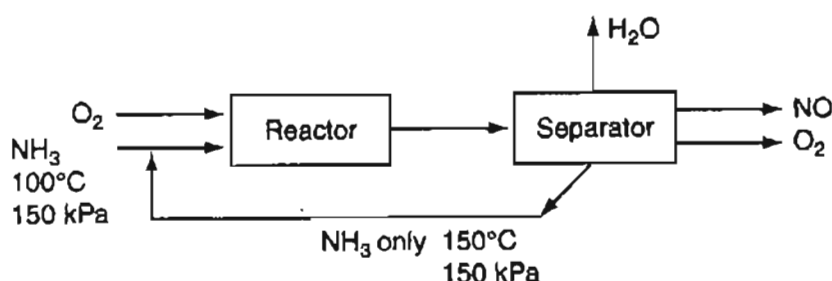


Figure P13.44

Calculate the m^3 of NH_3 recycled at 150°C and 150 kPa per m^3 of NH_3 fed at 100°C and 150 kPa .

- 13.45** Benzene (C_6H_6) is converted to cyclohexane (C_6H_{12}) by direct reaction with H_2 . The fresh feed to the process is 260 L/min of C_6H_6 plus 950 L/min of H_2 at 100°C and 150 kPa . The single pass conversion of H_2 in the reactor is 48% while the overall conversion of H_2 in the process is 75% . The recycle stream contains 90% H_2 and the remainder benzene (no cyclohexane). See Figure P13.45.

4.28

- Determine the molar flow rates of H_2 , C_6H_6 , and C_6H_{12} in the exiting product.
- Determine the volumetric flow rates of the components in the product stream if it exits at 100 kPa and 200°C .
- Determine the molar flow rate of the recycle stream, and the volumetric flow rate if the recycle stream is at 100°C and 100 kPa .

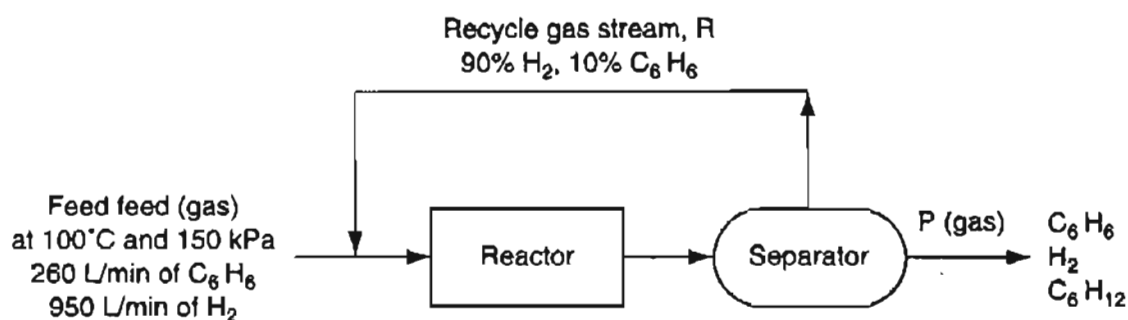


Figure P13.45

- 13.46** Pure ethylene (C_2H_4) and oxygen are fed to a process for the manufacture of ethylene oxide ($\text{C}_2\text{H}_4\text{O}$):

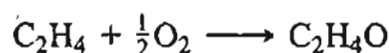
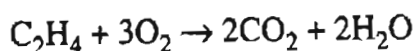


Figure P13.46 is the flow diagram for the process. The catalytic reactor operates at 300°C and 1.2 atm . At these conditions, single-pass measurements on the reactor show that 50% of the ethylene entering the reactor is consumed per pass, and of this, 70% is converted to ethylene oxide. The remainder of the ethylene reacts to form CO_2 and water.



For a daily production of 10,000 kg of ethylene oxide:

- Calculate the m^3/hr of total gas entering the reactor at SC if the ratio of the O_2 (g) fed to fresh C_2H_4 (g) is 3 to 2.
- Calculate the recycle ratio, m^3 at 10°C and 100 kPa of C_2H_4 recycled per m^3 at SC of fresh C_2H_4 fed;
- Calculate the m^3 of the mixture of O_2 , CO_2 and H_2O leaving the separator per day at 80°C and 100 kPa.

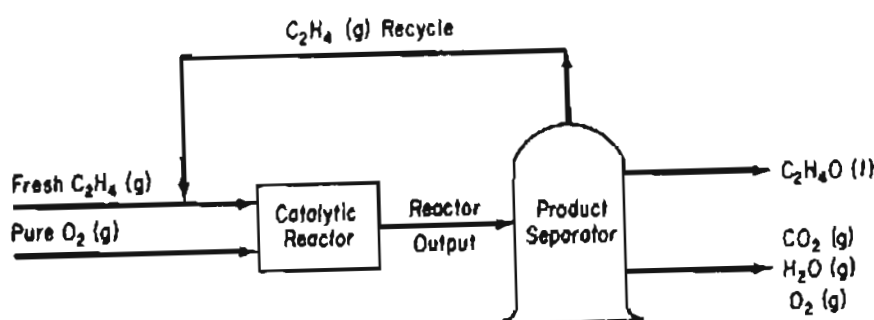
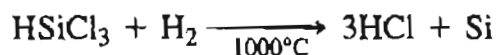


Figure P13.46

- **13.47** Three thousand cubic meters per day of a gas mixture containing methane and *n*-butane at 21°C enters an absorber tower. The partial pressures at these conditions are 103 kPa for methane and 586 kPa for *n*-butane. In the absorber, 80% of the butane is removed and the remaining gas leaves the tower at 38°C and a total pressure of 550 kPa. What is the volumetric flow rate of gas at the exit? How many moles per day of butane are removed from the gas in this process? Assume ideal behavior.
- **13.48** A heater burns normal butane ($n\text{-C}_4\text{H}_{10}$) using 40.0 percent excess air. Combustion is complete. The flue gas leaves the stack at a pressure of 100 kPa and a temperature of 260°C .
- Calculate the complete flue gas analysis.
 - What is the volume of the flue gas in cubic meter per kg mol of *n*-butane?
- **13.49** The majority of semiconductor chips used in the microelectronics industry are made of silicon doped with trace amounts of materials to enhance conductivity. The silicon initially must contain less than 20 parts per million (ppm) of impurities. Silicon rods are grown by the following chemical deposition reaction of trichlorosilane with hydrogen:



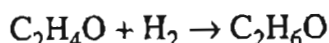
Assuming that the ideal gas law applies, what volume of hydrogen at 1000°C and 1 atm must be reacted to increase the diameter of a rod 1 m long from 1 cm to 10 cm? The density of solid silicon is 2.33 g/cm^3 .

- **13.50** An incinerator produces a dry exit gas of the following Orsat composition measured at 60°F and 30 inches of Hg absolute: 4.0% CO_2 , 26.0% CO , 2.0% CH_4 , 16.0% H_2 and 52.0% N_2 . A dry natural gas of the following (Orsat) composition: 80.5% CH_4 , 17.8%, C_2H_6 , and 1.7% N_2 is used at the rate of $1200 \text{ ft}^3/\text{min}$ at 60°F and 30 inches

of Hg absolute to burn the incineration off gas with air. The final products of combustion analyze on a dry basis: 12.2% CO₂, 0.7% CO, 2.4% O₂, and 84.7% N₂.

Calculate (a) the rate of flow in ft³/min of the incinerator exit gas at 60°F and 30 inches of Hg absolute on a dry basis, and (b) the rate of air flow in ft³/min, dry, at 80°F and 29.6 inches of Hg absolute.

- ✓**13.51 A gaseous mixture consisting of 50 mol % hydrogen and 50 mol % acetaldehyde (C₂H₄O) is initially contained in a rigid vessel at a total pressure of 760 mm Hg abs. The formation of ethanol (C₂H₆O) occurs according to



After a time it was noted that the total pressure in the rigid vessel had dropped to 700 mm Hg abs. Calculate the degree of completion of the reaction at that time using the following assumptions: (1) All reactants and products are in the gaseous state; and (2) the vessel and its contents were at the same temperature when the two pressures were measured.

- **13.52 Biomass (CH_{1.8}O_{0.5}N_{0.5}) can be converted to glycerol by anerobic (in the absence of air) reaction with ammonia and glucose. In one batch of reactants, 52.4 L of CO₂ measured at 300 K and 95 kPa was obtained per mole of glucose in the reactor. The molar stoichiometric ratio of nitrogen produced to ammonia reacted in the reaction equation is one to one, and the mol CO₂/mol C₆H₁₂O₅ = 2.

How much (in g mol) (a) glycerol was produced and (b) how much biomass reacted to produce the 52.4 L of CO₂?

- *13.53 The oxygen and carbon dioxide concentrations in the gas phase of a 10 L bioreactor operating in the steady-state control the dissolved oxygen and pH in the liquid phase where the biomass exists.
- If the rate of oxygen uptake by the liquid is 2.5×10^{-7} g mol/(1000 cells)(hr), and if the culture in the liquid phase contains 2.9×10^6 cells/mL, what is the rate of oxygen uptake in millimol/hr?
 - If the gas supplied to the gas phase is 45 L/hr containing 40% oxygen at 110 kPa and 25°C, what is the rate of oxygen supplied to the bioreactor in millimol/hr?
 - Will the oxygen concentration in the gas phase increase or decrease by the end of one hour compared to the initial oxygen concentration?

- *P13.54 When natural gas (mainly CH₄) is burned with 10 percent excess air, in addition to the main gaseous products of CO₂ and H₂O, other gaseous products result in minor quantities. The Environmental Protection Agency (EPA) lists the following data:

Emission Factors (kg/10⁶ m³ at SC)

	SO ₂	NO ₂	CO	CO ₂
Large utility boiler, uncontrolled	9.6	3040	1344	1.9×10^6
Large utility boiler, controlled gas recirculation	9.6	1600	1344	1.9×10^6
Residential furnace	9.6	1500	640	1.9×10^6

The data are based on 10^6 m^3 measured at SC of methane burned.

What is the approximate mole fraction of SO_2 , NO_2 , and CO (on a dry basis) for each class of combustion equipment?

- **P13.55** Estimate the emissions of each compound produced in m^3 measured at SC per metric ton (1000 kg) of No. 6 fuel oil burned in an oil-fired burner with no emission controls given the following data:

Pollution Emission Factors from the EPA, $\text{kg}/10^3 \text{ L}$ oil

SO_2	SO_3	NO_2	CO	CO_2	Particulate matter
19S^*	0.69S^*	8	0.6	3025	1.5

* S = weight percent sulfur

The No. 6 fuel oil contains 0.84% sulfur, and has a specific gravity of 0.86 at 15°C .

- *P13.56** The composition from Perry of No. 6 fuel oil with a specific gravity of 0.86 is in mass percent:

C	87.26
H	10.49
O	0.64
N	0.28
S	0.84
Ash	0.04

Compute the kg of each component per 10^3 L of oil, and compare the resulting emissions with those listed in the EPA analysis in Problem P13.55.

CHAPTER 14

REAL GASES: COMPRESSIBILITY

Your objectives in studying this chapter are to be able to:

1. Explain what the law of corresponding states means.
2. Define the critical state.
3. Calculate the reduced temperature, reduced pressure, and reduced ideal volume, and use any two of these three parameters to obtain the compressibility factor, z , from the compressibility charts.
4. Use compressibility factors and appropriate charts to predict the p - V - T behavior of a gas, or, given the required data, find a compressibility factor.
5. Calculate the compressibility factor z using the Pitzer acentric factor.
6. Use Kay's method of pseudocritical values to calculate the pseudo-reduced values, and predict p , V , T , and n via the compressibility factor.

*Predicting gas features has appeal
By a law that appears to be real
But somehow the law
Seems to have flaws
Because gases are rarely ideal*

DMH

Looking Ahead

In this chapter we explain how the critical properties of gases can be employed to facilitate the calculation of a compressibility factor, a factor that transforms the ideal gas law into a relation that can be used to solve for p , V , n , and T for single- and multi-component real gases.

Main Concepts

14.1 Corresponding States

When gases do not conform to the assumptions underlying ideality that were explained in Chapter 13, we call them **real gases**. For example, if you compress argon to 1000 atm in a chamber with a viewport, the argon will have about the same density as water (but it is still a gas), and you can float a material in the argon that floats on water. You cannot apply the ideal gas law under such conditions. Figure 14.1 shows the error involved in using the ideal gas law to predict p - \hat{V} - T properties for steam.

In the attempt to devise some truly universal gas law that predicts well at low and high pressures, the idea of corresponding states was developed. Early experimenters found that at the critical point all substances are in approximately the same state of molecular dispersion. Consequently, it was felt that their thermodynamic and physical properties should be similar. The **law of corresponding states** expresses the idea that in the critical state all substances should behave alike.

What does the **critical state (point)** mean? For a pure component it means the maximum temperature and corresponding pressure at which liquid and vapor can coexist. You can find many definitions, but the one most suitable for general use with pure component systems as well as with mixtures of gases is the following:

The critical state for the gas-liquid transition is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.

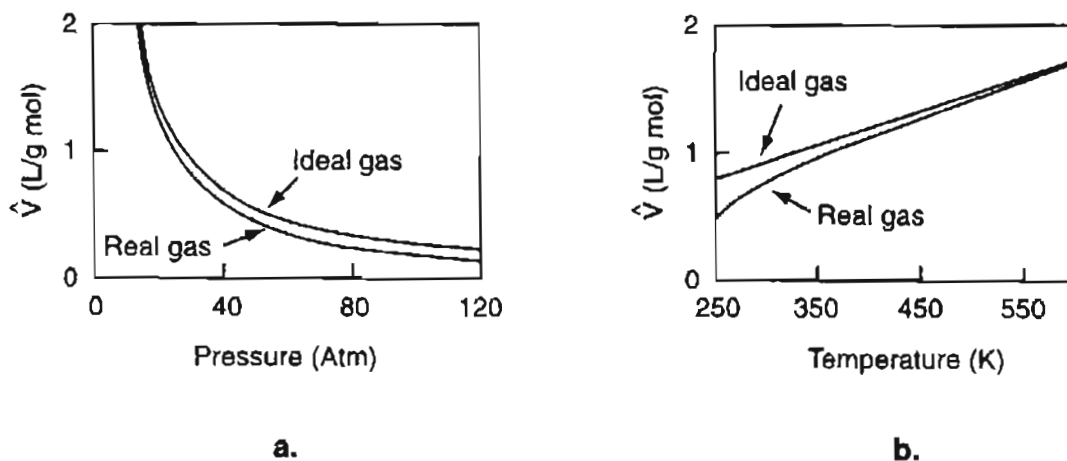


Figure 14.1 Graph of the measured specific volume \hat{V} of steam as a function of (a) the pressure and (b) the temperature contrasted with predictions by the ideal gas law. Note that the deviations at high pressure and low temperature are relatively quite large.

14.2 Critical State

One way to determine the critical state is by acoustic measurements because the speed of sound in a fluid drops to a minimum when the fluid is in the critical state. In fact, in 1822 acoustic effects were exploited unwittingly by Cagniard de la Tour when he heated alcohol in a sealed gun barrel and listened to the musket ball rolling around. Figure 14.2 shows the measurements by Andrews in 1863 of the pressure versus the specific volume for CO_2 .

Note the point C at 31°C is the highest temperature at which liquid and gaseous CO_2 can coexist in equilibrium. Above 31°C only fluid exists, so that the critical temperature for CO_2 is 31°C (304K). The corresponding pressure is 72.9 atm (7385 kPa). Also note that at higher temperatures, such as 50°C , the data can be represented by the ideal gas law because $pV = \text{constant}$, a hyperbola.

You can find experimental values of the critical temperature (T_c) and the critical pressure (p_c) for various compounds in Appendix D and on the CD that accompanies this book. If you cannot find a desired critical value in this text or in a handbook, you can always consult Poling et al. (refer to references at the end for this chapter), which describes and evaluates methods of estimating critical constants for various compounds.

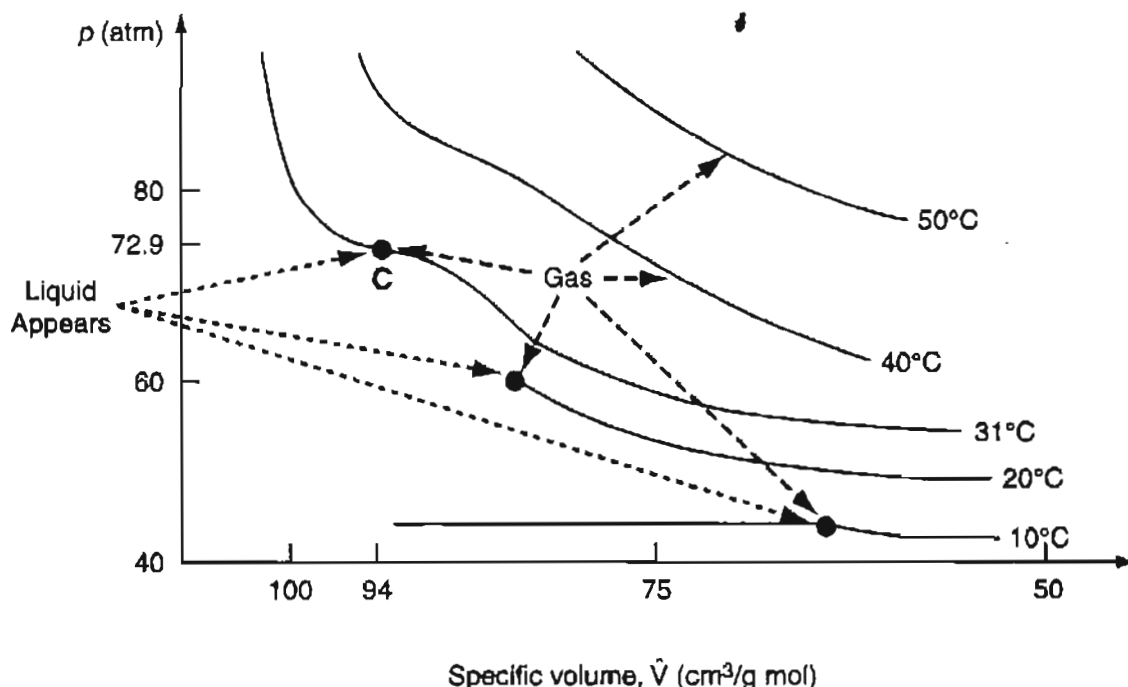


Figure 14.2 Experimental measurements of carbon dioxide by Andrews. The solid lines represent smoothed data. C is the highest temperature at which any liquid exists. At the solid dots liquid and vapor coexist.

A **supercritical fluid** is a compound in a state above its critical point. Supercritical fluids are used to replace solvents such as trichloroethylene and methylene chloride, the emissions from which, and the contact with, have been severely limited. For example, coffee decaffeination, the removal of cholesterol from egg yolk with CO_2 , the production of vanilla extract, and the destruction of undesirable organic compounds all can take place using supercritical water. Oxidation in supercritical water has been shown to destroy 99.99999% of all of the major types of toxic agents present in chemical weapons, which are being eliminated.

14.3 Reduced Variables

Other terms with which you should become familiar are the **reduced variables**. These are **corrected**, or *normalized*, conditions of temperature, pressure, or volume, normalized (divided) by their respective critical conditions, as follows:

$$T_r = \frac{T}{T_c}$$

$$p_r = \frac{p}{p_c}$$

$$V_r = \frac{\hat{V}}{\hat{V}_c}$$

In theory, the law of corresponding states indicates that any compound should have the same reduced volume at the same reduced temperature and reduced pressure so that a universal gas law might be

$$P_r \hat{V}_r = k T_r \quad (14.1)$$

Unfortunately Equation (14.1) does not make accurate predictions universally. You can check this conclusion by selecting a compound such as water, applying Equation (14.1) at some low temperature and high pressure to calculate \hat{V} , and comparing your results with the value obtained for \hat{V} for the corresponding conditions from the steam tables that are in the folder in the back of this book.

14.4 Compressibility

How can the ideas presented above be used? One common way is to modify the ideal gas law by inserting an adjustable coefficient z , the **compressibility factor**, a factor that compensates for the nonideality of the gas, and can be looked at as a

measure of nonideality. Thus, the ideal gas law is turned into a real gas law, a **generalized equation of state**.

$$pV = znRT \quad (14.2)$$

or

$$p\hat{V} = zRT \quad (14.2a)$$

One way to look at z is to consider it to be a factor that makes Equation (14.2) an equality. Although we treat only gases in this chapter, the same idea has been applied to liquids.

If you plan on using Equation (14.2), where can you find the values of z to use in it? Equations exist in the literature for specific compounds and classes of compounds, such as those found in petroleum refining. Refer to the references at the end of this chapter. But you will find graphs or tables of z to be convenient sources for

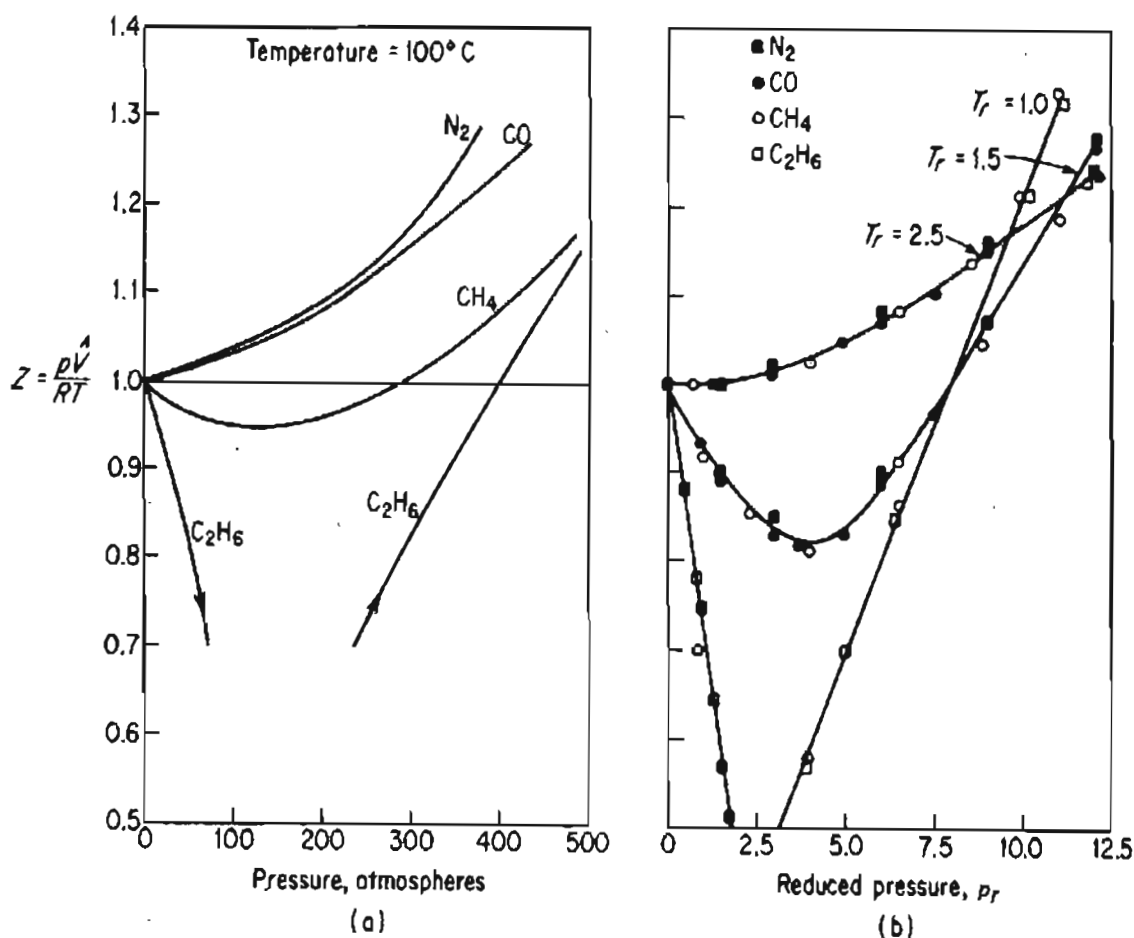


Figure 14.3 (a) Compressibility factor at 100°C for several gases as a function of pressure; (b) compressibility factor for several gases as a function of reduced temperature and reduced pressure.

values of z . If the compressibility factor is plotted for a given temperature against the pressure for different gases, figures like Figure 14.3a result. However, if the compressibility is plotted against the reduced pressure as a function of the reduced temperature, then for most gases the compressibility values at the same reduced temperature and reduced pressure fall at about the same point, as illustrated in Figure 14.3b.

14.5 Compressibility Charts

Because of the generalization feature shown in Figure 14.3b, you can use what is called the generalized compressibility factor z for your gas calculations. Figures 14.4a and 14.4b shows two examples of the **generalized compressibility factor charts**, or z -factor charts, prepared by Nelson and Obert.* These charts are based on data for 30 gases. Figure 14.4(a) represents z for 26 gases (excluding H_2 , He, NH_3 , and H_2O) with a maximum deviation of 1%, and H_2 and H_2O within a deviation of 1.5%. Figure 14.4(b) is for nine gases and errors can be as high as 5%. Note that the vertical axis is not z but zT_r in Figure 14.4(b). To use the charts for H_2 and He (only), make corrections to the actual constants to get **pseudocritical** constants

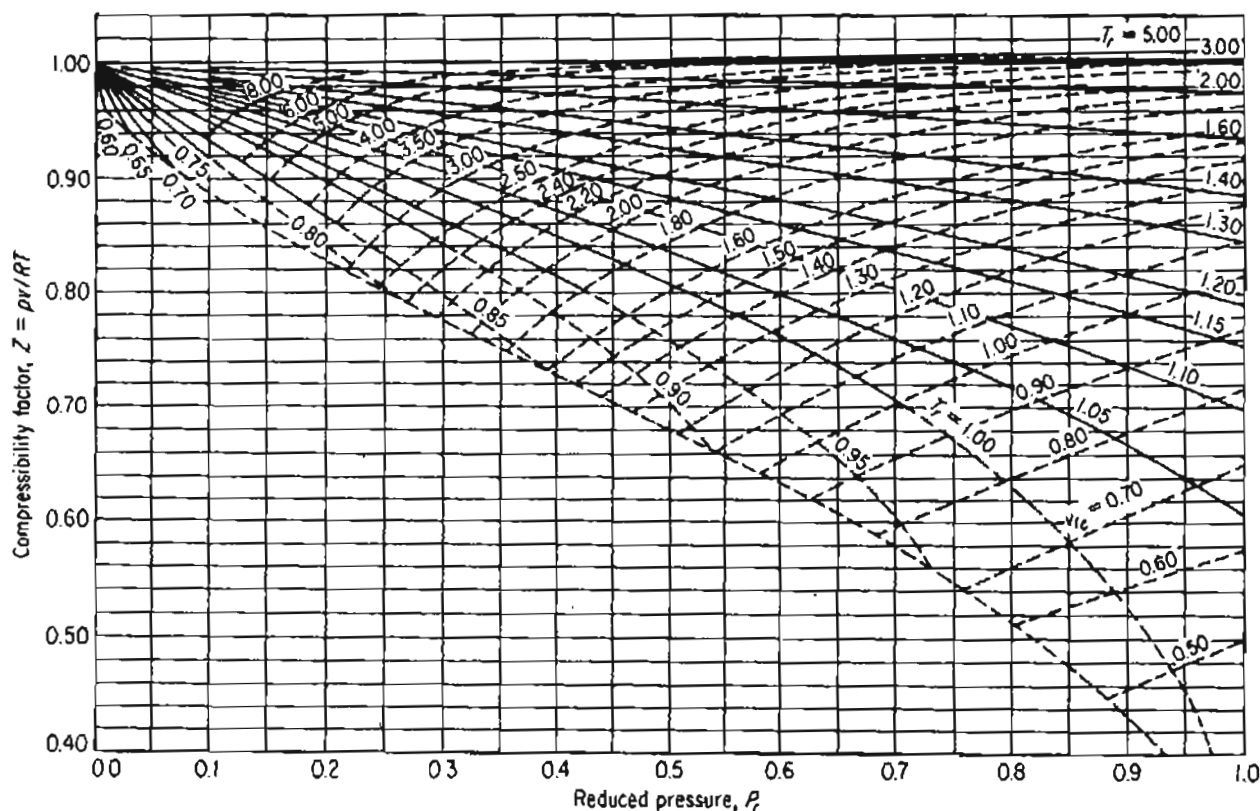


Figure 14.4a Generalized compressibility chart for lower pressures showing z as a function of p_r , T_r , and \hat{V}_{r1} .

*Nelson, L.C., and E.F. Obert. *Chem. Eng.*, v. 61, No. 7, pp. 203–208 (1954). Figures 14.4(a) and 14.4(b) include data reported by P.E. Liley. *Chem. Eng.*, p. 123 (July 20, 1987).

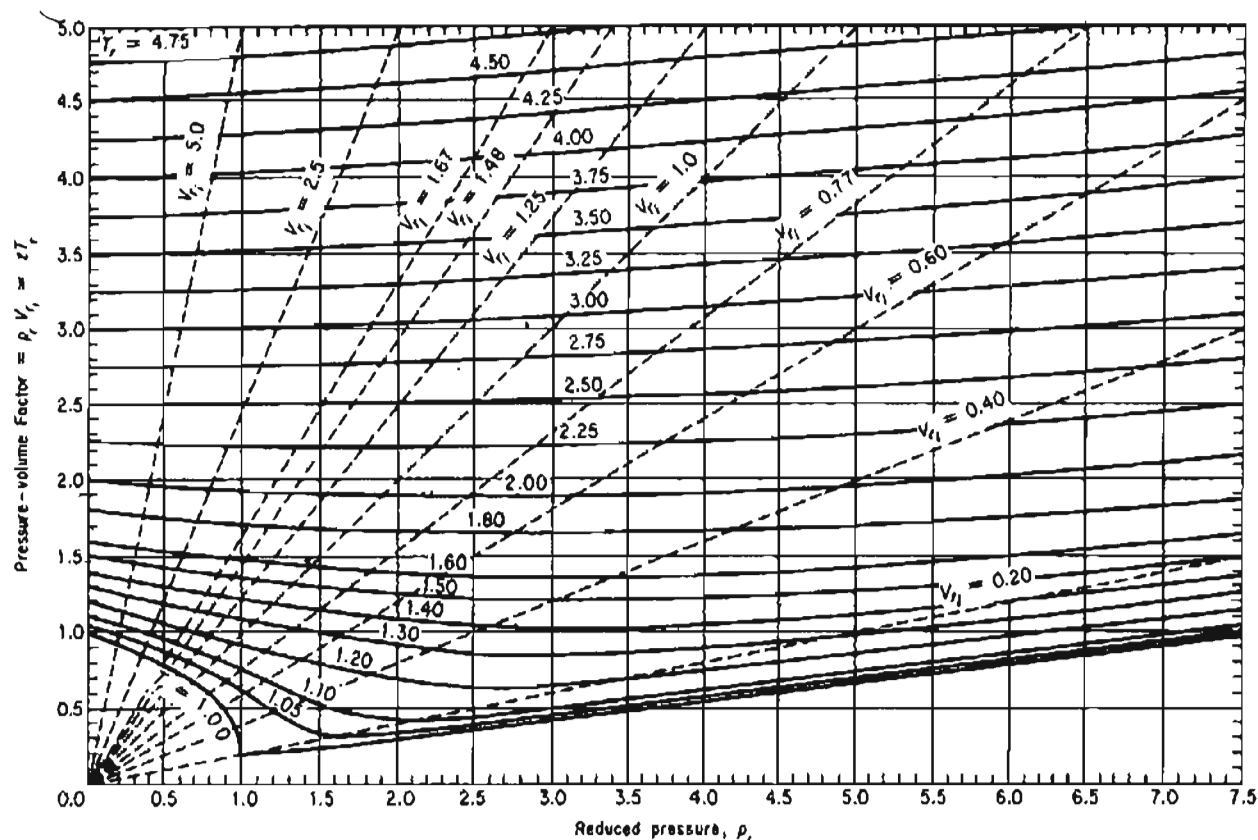


Figure 14.4b Generalized compressibility chart for higher values of p_r

$$T'_c = T_c + 8 \text{ K}$$

$$p'_c = p_c + 8 \text{ atm}$$

and then you can use Figures 14.4a and 14.4b for these two gases using the pseudo-critical constants as replacements for their true values. You will find these two charts and additional charts for other ranges of p_r and T_r on the CD that accompanies this book in a format that can be expanded to get better accuracy.

Instead of the reduced specific volume, a third parameter shown on the charts is the dimensionless ideal reduced volume defined by

$$V_{r,i} = \frac{\hat{V}}{\hat{V}_{c,i}}$$

where $\hat{V}_{c,i}$ is the ideal critical volume (not the experimental value of the critical volume), and is calculated from

$$\hat{V}_{c,i} = \frac{RT_c}{p_c} \quad (14.3)$$

Both $\hat{V}_{c,i}$ and $V_{r,i}$ are easy to calculate since T_c and p_c are presumed known or can be estimated for a compound. The development of the generalized compressibility

charts is of considerable practical as well as pedagogical value because their existence enables you to make engineering calculations with considerable ease, and also permits the development of thermodynamic functions for gases for which no experimental data are available.

Frequently Asked Questions

1. What is in the blank region in Figure 14.4a below the curves for T_r and \hat{V}_r ? The blank region corresponds to a different phase—a liquid.
2. Will $p\hat{V} = zRT$ work for a liquid phase? Yes, but relations to calculate z accurately are more complex than those for the gas phase. Also, liquids are not very compressible so that for our purposes we can ignore p - \hat{V} - T relations for liquids.
3. Why should I use $p\hat{V} = zRT$ when I can look up the data needed in a handbook or on the Web? Although considerable data exists, you can use $p\hat{V} = zRT$ to evaluate the accuracy of the data and interpolate within data points. If you do not have data in the range you want, use of $p\hat{V} = zRT$ is the best method of extrapolation. Finally, you may not have any data for the gas of interest.

EXAMPLE 14.1 Use of the Compressibility Factor to Calculate a Specific Volume

In spreading liquid ammonia fertilizer, the charges for the amount of NH_3 used are based on the time involved plus the pounds of NH_3 injected into the soil. After the liquid has been spread, there is still some ammonia left in the source tank (volume = 120 ft³), but in the form of a gas. Suppose that your weight tally, which is obtained by difference, shows a net weight of 125 lb of NH_3 left in the tank at 292 psig. Because the tank is sitting in the sun, the temperature in the tank is 125°F.

Your boss complains that his calculations show that the specific volume of the NH_3 gas is 1.20 ft³/lb, and hence that there are only 100 lb of NH_3 in the tank. Could he be correct? See Figure E14.1

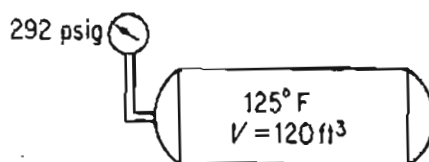


Figure E14.1

Solution

Basis: 1 lb of NH_3

You can apply $pV = znRT$ to calculate n and check the amount of NH_3 in the tank. Apparently, your boss used the ideal gas law in getting his figure of 1.20 ft³/lb of NH_3 gas:

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})} \quad p = 292 + 14.7 = 306.7 \text{ psia}$$

$$T = 125^\circ\text{F} + 460 = 585^\circ\text{R} \quad n = \frac{1 \text{ lb}}{17 \text{ lb/lb mol}}$$

$$V = \frac{nRT}{p} = \frac{\frac{1}{17}(10.73)(585)}{306.7} = 1.20 \text{ ft}^3 \text{ per lb}$$

However, he should have included the compressibility factor in the gas law because NH_3 does not behave as an ideal gas under the observed conditions of temperature and pressure. Let us again compute the mass of gas in the tank, this time using

$$pV = znRT$$

You know all of the values of the variables in the equation except z . The additional information needed (taken from Appendix D or the CD) is

$$T_c = 405.5\text{K} \Rightarrow 729.9^\circ\text{R}$$

$$p_c = 111.3 \text{ atm} \Rightarrow 1636 \text{ psia}$$

Then since z is a function of T_r and p_r ,

$$T_r = \frac{T}{T_c} = \frac{585^\circ\text{R}}{729.9^\circ\text{R}} = 0.801$$

$$p_r = \frac{p}{p_c} = \frac{306.7 \text{ psia}}{1636 \text{ psia}} = 0.187$$

From the Nelson and Obert chart, Figure 14.4(a), you can read $z \approx 0.855$. (The value may be somewhat in error because ammonia was not one of the gases included in the preparation of the figure.) Now V can be calculated from the ratio of $pV_{\text{real}} = z_{\text{real}} nRT$ to $pV_{\text{ideal}} = z_{\text{ideal}} nRT$, the net result of which is

$$\frac{\hat{V}_{\text{real}}}{\hat{V}_{\text{ideal}}} = \frac{z_{\text{real}}}{z_{\text{ideal}}}$$

On the basis of 1 lb NH_3

$$\hat{V}_{\text{real}} = \frac{1.20 \text{ ft}^3 \text{ ideal}}{1 \text{ lb}} \left| \frac{0.855}{1} \right| = 1.03 \text{ ft}^3 \text{ per lb } \text{NH}_3$$

On the basis of 120 ft³ in the tank

$$\frac{1 \text{ lb NH}_3}{1.03 \text{ ft}^3} \left| \frac{120 \text{ ft}^3}{1} \right| = 117 \text{ lb NH}_3$$

Certainly 117 lb is a more realistic figure than 100 lb, and it is easily possible to be in error by 8 lb if the residual weight of NH₃ in the tank is determined by difference. As a matter of interest, as an alternative to making the calculations, you could look up the specific volume of NH₃ at the conditions in the tank in a handbook. You would find that $\hat{V} = 0.973 \text{ ft}^3/\text{lb}$, and hence the compressibility factor calculation yielded a specific volume with an error of about 5.9% versus an error of 23% using the ideal gas law.

EXAMPLE 14.2 Use of the Compressibility Factor to Calculate a Pressure

Liquid oxygen is used in the steel industry, in the chemical industry, in hospitals, as a rocket fuel oxidant, and for wastewater treatment as well as many other applications. A hospital tank of 0.0284 m³ volume is filled with 3.500 kg of liquid O₂ that will vaporize at -25°C. Will the pressure in the tank exceed the safety limit of the tank specified as 10⁴ kPa?

Solution

Basis: 3.500 kg O₂

You can find from Appendix D or the CD that for oxygen

$$T_c = 154.4 \text{ K}$$

$$p_c = 49.7 \text{ atm} \Rightarrow 5,035 \text{ kPa}$$

However, you cannot proceed to solve this problem in exactly the same way as you did the preceding problem because you do not know the pressure of the O₂ in the tank to begin with. Thus, you need to use the pseudoparameter, V_{r_i} , that is available as a parameter on the Nelson and Obert charts.

First, calculate

$$\hat{V}(\text{specific molal volume}) = \frac{0.0284 \text{ m}^3}{3.500 \text{ kg}} \left| \frac{32 \text{ kg}}{1 \text{ kg mol}} \right| = 0.260 \text{ m}^3/\text{kg mol}$$

Note that the *specific molar volume* must be used in calculating V_{r_i} since \hat{V}_{c_i} is a volume per mole.

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} = \frac{8.314(\text{m}^3)(\text{kPa})}{(\text{kg mol})(\text{K})} \left| \frac{154.4 \text{ K}}{5,035 \text{ kPa}} \right| = 0.255 \frac{\text{m}^3}{\text{kg mol}}$$

Then

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}} = \frac{0.260}{0.255} = 1.02$$

Now you know the values of two parameters, V_{r_i} and

$$T_r = \frac{248 \text{ K}}{154.4 \text{ K}} = 1.61$$

From the Nelson and Obert chart (Figure 14.4(b)) you can read

$$p_r = 1.43$$

Then

$$\begin{aligned} p &= p_r p_c \\ &= 1.43 (5,035) = 7200 \text{ kPa} \end{aligned}$$

The pressure of 10^4 kPa will not be exceeded. Even at room temperature the pressure will be less than 10^4 kPa.

14.6 Calculating the Compressibility Factor Using the Pitzer Factors z^0 and z^1

Several methods have appeared in the literature and in computer codes to calculate z via an equation in order to obtain more accurate values of z than can be obtained from charts. Equation (14.4) employs the Pitzer acentric factor, ω

$$z = z^0 + z^1 \omega \quad (14.4)$$

where z^0 and z^1 are listed in tables in Appendix C as a function of T_r and p_r , and ω is unique for each compound, and can be found in the CD that accompanies this book. Table 14.1 is an abbreviated table of the acentric factors from Pitzer.

The acentric factor ω indicates the degree of acentricity or nonsphericity of a molecule. For helium and argon, ω is equal to zero. For higher molecular weight hydrocarbons and for molecules with increased polarity, the value of ω increases.

Table 14.2 lists the value of z obtained for ethylene (C_2H_4) at two conditions by three different methods: (a) by Equation (14.4), (b) from the generalized compressibility charts, and (c) from the ideal gas law. The three values are compared with the experimental value (from *Perry's Handbook*, 7th edition).

If you redo Example 14.1 using Equation (14.4) with the Pitzer acentric factor for $p_r = 0.187$ and $T_r = 0.801$, by linear interpolation of data in the tables in Appendix C, you will find that $z^0 = 0.864$ and $z^1 = -0.103$ so that $z = 0.838$, and the lb of $\text{NH}_3 = 119$. If you want to redo Example 14.2 using Equation (14.4), you will have

TABLE 14.1 Values of the Pitzer* Acentric Factor

Compound	Acentric Factor	Compound	Acentric Factor
Acetone	0.309	Hydrogen sulfide	0.100
Benzene	0.212	Methane	0.008
Ammonia	0.250	Methanol	0.559
Argon	0.000	n-butane	0.193
Carbon dioxide	0.225	n-pentane	0.251
Carbon monoxide	0.049	Nitric oxide	0.607
Chlorine	0.073	Nitrogen	0.040
Ethane	0.098	Oxygen	0.021
Ethanol	0.635	Propane	0.152
Ethylene	0.089	Propylene	0.148
Freon-12	0.176	Sulfur dioxide	0.251
Hydrogen	-0.220	Water vapor	0.344

*Pitzer, K.S., *J. Am. Chem. Soc.* 77 (1955):3427.

to use a trial-and-error solution because you do not know p at the start. What you do is to assume a sequence of values of p , calculate the related sequence of values of p_r , and next calculate the associated sequence of values of z and then \hat{V} . When you find the value of the specific volume that matches the value specified in the problem, you have identified the correct p_r and can then calculate $p = p_c p_r$.

TABLE 14.2 A Comparison of Values of the Compressibility Factor z for Ethylene Determined via Three Different Methods with the Experimental Values

	Specified Conditions*			
	At 350K and 5 atm		At 300 K and 30 atm	
	z	% deviation	z	% deviation
Experimental	0.983	—	0.812	—
Compressibility chart	0.982	0.0	0.815	0.0
Ideal gas law	1	1.8	1	23.1
Equation (14.4)	0.983	0.0	0.812	0.0
	$z^0 = 0.983$		$z^0 = 0.812$	
	$z^1 = 0.00476$		$z^1 = 0.0131$	

* $\omega = 0.089$, $T_c = 282.8\text{K}$, $p_c = 50.5\text{ atm}$, z^0 and z^1 are from the tables in Appendix C.

*Kay, W.B. "Density of Hydrocarbon Gases and Vapors at High Temperature and Pressure," *Ind. Eng. Chem.* 28, 1014–1019 (1936).

14.7 Real Gas Mixtures

How can you apply the concept of compressibility to problems involving gas mixtures? Each component in the mixture will have different critical properties. Numerous ways have been proposed to properly weigh the critical properties so that an appropriate reduced temperature and pressure can be used to obtain z . Refer to the references at the end of this chapter for some examples. One simple way that is reasonably accurate, at least for our purposes, is Kay's method.*

In Kay's method, **pseudocritical** values for mixtures of gases are calculated on the assumption that each component in the mixture contributes to the pseudocritical value in the same proportion as the mol fraction of that component in the gas. Thus, the pseudocritical values are computed as follows:

$$p'_c = p_{cA}y_A + p_{cB}y_B + \dots \quad (14.5)$$

$$T'_c = T_{cA}y_A + T_{cB}y_B + \dots \quad (14.6)$$

where y_i is the mole fraction, p'_c is the pseudocritical pressure and T'_c is the pseudocritical temperature. You can see that these are linearly weighted mole average pseudocritical properties. As an example of how the averaging works, look at Figure 14.5, which compares the true critical values of a gaseous mixture of CO_2 and SO_2 with the respective pseudocritical values. The respective pseudoreduced variables are

$$p'_r = \frac{p}{p'_c}$$

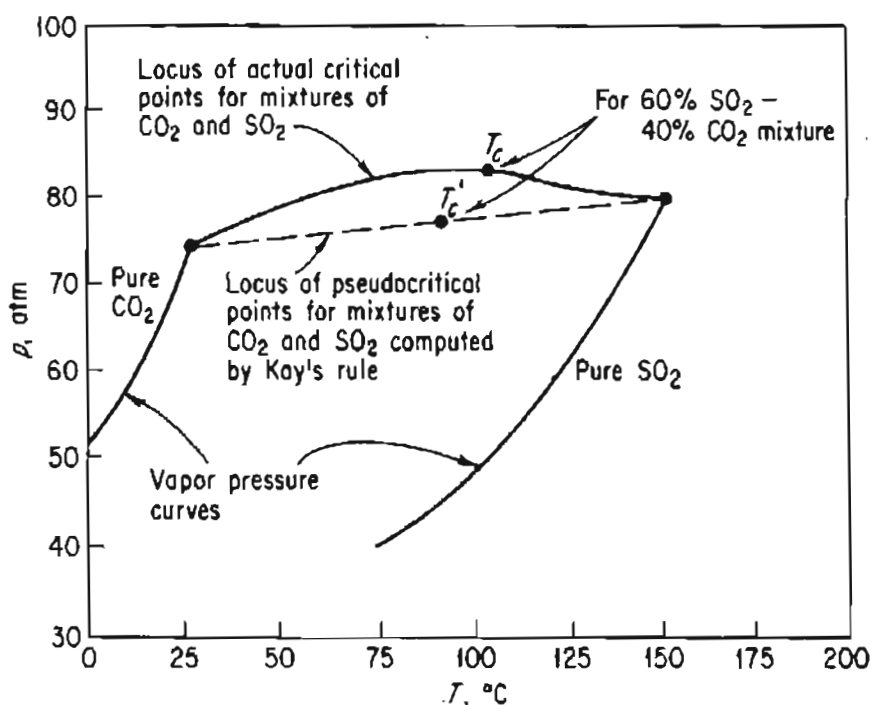


Figure 14.5 Critical and pseudocritical points for mixtures of CO_2 and SO_2 .

$$T'_r = \frac{T}{T'_c}$$

Kay's method is known as a two-parameter rule since only p_c and T_c for each component are involved in the calculation of z . If a third parameter such as z_c , or the Pitzer acentric factor, or \hat{V}_{ci} is included in the determination of the compressibility factor, then you would have a three-parameter rule. Other pseudocritical methods with additional parameters provide better accuracy in predicting p - V - T properties than Kay's method, but Kay's method can suffice for our work, and it is easy to use.

EXAMPLE 14.3 Calculation of p - V - T Properties for a Real Gas Mixture

A gaseous mixture has the following composition (in mole percent):

Methane, CH ₄	20
Ethylene, C ₂ H ₄	30
Nitrogen, N ₂	50

at 90 atm pressure and 100°C. Compare the volume per mole as computed by the methods of: (a) the ideal gas law and (b) the pseudoreduced technique (Kay's method).

Solution

Basis: 1 g mol of gas mixture

Additional data needed are:

Component	T_c (K)	p_c (atm)
CH ₄	191	45.8
C ₂ H ₄	283	50.5
N ₂	126	33.5

$$R = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

a. Ideal gas law:

$$\hat{V} = \frac{RT}{p} = \frac{1(82.06)(373)}{90} = 340 \text{ cm}^3/\text{g mol at 90 atm and 373 K}$$

b. According to Kay's method, you first calculate the pseudocritical values for the mixture

$$\begin{aligned} p'_c &= p_{cA}y_A + p_{cB}y_B + p_{cC}y_C = (45.8)(0.2) + (50.5)(0.3) + (33.5)(0.5) \\ &= 41.1 \text{ atm} \end{aligned}$$

$$T'_c = T_{cA}y_A + T_{cB}y_B + T_{cC}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5) = 186 \text{ K}$$

Then you calculate the pseudoreduced values for the mixture

$$p'_r = \frac{p}{p'_c} = \frac{90}{41.2} = 2.19, \quad T'_r = \frac{T}{T'_c} = \frac{373}{186} = 2.01,$$

With the aid of these two parameters you can find from Figure 14.4b that $zT'_r = 1.91$ and thus $z = 0.95$. Then

$$\hat{V} = \frac{zRT}{p} = \frac{0.95(1)(82.06)(373)}{90} = 323 \text{ cm}^3/\text{g mol at 90 atm and 373 K}$$

If you decided to use Equation (14.4) to calculate z for the mixture, how might you average z^0 , z^1 , and ω ?

In instances in which the temperature or pressure of a gas mixture is unknown, to avoid a trial-and-error solution using the generalized compressibility charts, you can compute the pseudocritical ideal volume and a **pseudoreduced ideal volume** V'_{ri} , thus

$$\hat{V}'_{ci} = \frac{RT'_c}{p'_c} \quad \text{and} \quad V'_{ri} = \frac{\hat{V}}{\hat{V}'_{ci}}$$

V'_{ri} can be used in lieu of p'_r or T'_r in the compressibility charts.

SELF-ASSESSMENT TEST

Questions

- What is the pseudocritical volume? What is the advantage of using V'_{ci} ?
- Answer the following questions true or false.
 - Two fluids, which have the same values of reduced temperature and pressure and the same reduced volume, are said to be in corresponding states.
 - It is expected that all gases will have the same z at a specified T_r and p_r . Thus a correlation of z in terms of T_r and p_r would apply to all gases.
 - The Law of Corresponding States states that at the critical state (T_c, p_c) all substances should behave alike.
 - The critical state of a substance is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.
 - Any substance (in theory) by the Law of Corresponding States should have the same reduced volume at the same reduced T_r and p_r .

- f. The equation $pV = znRT$ cannot be used for ideal gases.
 - g. By definition a fluid becomes supercritical when its temperature and pressure exceed the critical point.
 - h. Phase boundaries do not exist under supercritical conditions.
 - i. For some gases under normal conditions, and for most gases under conditions of high pressure, values of the gas properties that might be obtained using the ideal gas law would be at wide variance with the experimental evidence.
3. Explain the meaning of the following equation for the compressibility factor

$$z = f(T_r, p_r)$$

4. What is the value of z at $p = 0$?

Problems

1. Calculate the compressibility factor z , and determine whether or not the following gases can be treated as ideal, at the listed temperature and pressure: (a) water at $1,000^\circ\text{C}$ and $2,000\text{ kPa}$; (b) oxygen at 35°C and $1,500\text{ kPa}$; and (c) methane at 10°C and $1,000\text{ kPa}$.
2. In a proposed low pollution vehicle burning H_2 with O_2 , the respective gases are to be stored in two separate tanks at 2000 psia . The vehicle has to operate from -40 to 130°F .
 - a. Is the ideal gas law a sufficiently good approximation to use in the design of these tanks?
 - b. A practical operating range requires that 3 lb_m of hydrogen be stored. How large must the hydrogen tank be if the pressure is not to exceed 2000 psia ?
 - c. The H_2/O_2 ratio is 2 on a molar basis in the proposed fuel. How large must the oxygen tank be?
3. A carbon dioxide fire extinguisher has a volume of 40 L and is to be charged to a pressure of 20 atm at a storage temperature of 20°C . Determine the mass in kilograms of CO_2 at 1 atm .
4. Calculate the pressure of 4.00 g mol CO_2 contained in a $6.25 \times 10^{-3}\text{ m}^3$ fire extinguisher at 25°C .
5. One pound mole of a mixture containing $0.400\text{ lb mol of N}_2$ and $0.600\text{ lb mol C}_2\text{H}_4$ at 50°C occupies a volume of 1.44 ft^3 . What is the pressure in the vessel? Compute your answer by Kay's method.

Thought Problems

1. At a swimming pool the pressure regulator attached to the chlorine cylinder did not seem to function properly, hence the valve on the cylinder was closed. After standing for 8 months someone disconnected the regulator to replace it, and chlorine gas spurted into his face. He and three other people had to be hospitalized. What happened to cause the accident?
2. Pressure vessels and rigid piping have to be protected against overpressure by using safety devices. For example, when liquid is trapped within a rigid piping system, it ex-

pands, and a small expansion caused by a temperature increase will produce a large pressure rise in the system in the vapor above the liquid. What happens in a space containing 400 L of liquid and a gas bubble of 4.0 L with an initial pressure of 1 atm when the liquid expands 1% so that the gas volume is compressed? Will the piping system fail?

3. The sum of the mass fractions for an ideal gas mixture is equal to 1. Is the sum also equal to 1 for a real gas mixture?
4. Municipal sludge is being converted to sterile ash and readily biodegradable liquid effluent in a mile-deep well at Longmont, Colorado. The process reduces the chemical oxygen demand, that is, the required oxygen to oxidize organic compounds in the sludge, by up to 68%, and destroys all living organisms. Tubes of appropriate diameter are placed in the well to create an annual space for two-phase flow down and up the well. Oxidation takes place at the bottom of the well with air. Why is it advantageous to oxidize the sludge at the bottom of the well rather than in a pond at the surface?

Discussion Problems

1. A letter to the editor was headed "Not Sold on Hydrogen." In part it said:

Your innovative story "Fuel Cells: A Lot of Hot Air?" concerned me. Hydrogen under pressure is difficult to contain. Leaks are difficult to detect, and you need to obtain virtual zero leakage. Hydrogen is explosive and flammable, and burns with an invisible flame. Finally, your economics do not address the entire process from beginning to end, and come to less than realistic conclusions.

Comment on the points that the author of the letter makes. Do they damage the potential of hydrogen-based fuel cells? In what aspects is he correct, and in what aspects wrong?

2. In the early 1970s it was believed that geopressured brines might contain appreciable potential for electric power production because the thermal and kinetic energy of the waters represents approximately 50% of the total energy in the fluids. However, field tests have indicated that temperatures at 15,000 feet are usually in the range of 275 to 300°F, making electricity production marginal.

However, the brines are saturated with natural gas. Ten test wells have been tested in coastal Texas and Louisiana at an average cost of \$2 million each. Test results have been mixed. Brine salinities have ranged from 13,000 to 191,000 ppm. Most tests indicate gas at or near saturation levels. Temperatures have ranged from 237 to 307°F and formation pressures from 11,050 to 13,700 psia. Flow rates have ranged from 13,000 to 29,000 barrels per day of water. Because natural gas content is proportional to temperature and pressure but inversely proportional to salinity, the natural gas content in design wells ranges from 19 to 50 standard cubic feet per barrel. All of the wells have indicated some carbon dioxide (CO_2) in the gases produced. The concentration seems to be correlative with temperature, ranging from 4 to 9% of total gas content. The CO_2 has the potential to cause scaling problems, requiring use of inhibitors. Reservoir limits are very large. Transient pressure testing on two wells indicates no barriers to an outer limit of about 4 miles.

Is recovery of natural gas from such wells a viable source of energy? Prepare a brief report that includes economic, engineering, and environmental considerations for the proposed gas production.

Looking Back

In this chapter we described the law of corresponding states and the reduced variables of temperatures and pressure. These concepts led to the idea of the compressibility factor that could be used in the ideal gas law to generalize it for application to real gases. Both charts and equations were used to estimate z . In addition, we described how to apply Kay's method (the pseudocritical method) to predict p , V , n , and T in real gas mixtures.

GLOSSARY OF NEW WORDS

Acentric factor A parameter that indicates the degree of nonsphericity of a molecule.

Compressibility charts Graphs of the compressibility factor as a function of reduced temperature, reduced pressure, and ideal reduced volume.

Compressibility factor A factor that is introduced into the ideal gas law to compensate for the nonideality of a gas.

Corrected Normalized.

Corresponding states Any gas should have the same reduced volume at the same reduced temperature and reduced pressure.

Critical state The set of physical conditions at which the density and other properties of liquid and vapor become identical.

Generalized compressibility chart See Compressibility charts.

Generalized equation of state The ideal gas law converted to a real gas law by inserting a compressibility factor.

Ideal critical volume $\hat{V}_{c,i} = RT_c/p_c$

Ideal reduced volume $V_{r,i} = \hat{V}/\hat{V}_{c,i}$

Kay's method Procedure for calculating the compressibility factor for a mixture of gases.

Law of corresponding states See Corresponding states.

Pitzer acentric factor See Acentric factor.

Pseudocritical Temperatures, pressures, and /or specific volumes adjusted to be used with charts or equations used to calculate the compressibility factor.

Real gases Gases whose behavior does not conform to the assumptions underlying ideality.

Reduced variables Corrected or normalized conditions of temperature, pressure, and volume, normalized by their respective critical conditions.

Supercritical fluid Material in a state above its critical point.

SUPPLEMENTARY REFERENCES

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PROBLEMS

- *14.1 Seven pounds of N_2 are stored in a cylinder 0.75 ft³ volume at 120°F. Calculate the pressure in the cylinder in atmospheres:
- Assuming N_2 to be an ideal gas.
 - Assuming N_2 is a real gas and using compressibility factors.
- / *14.2 Two gram moles of ethylene (C_2H_4) occupy 418 cm³ at 95°C. Calculate the pressure. (Under these conditions ethylene is a nonideal gas.) Data: $T_c = 283.1\text{K}$, $p_c = 50.5\text{ atm}$, $\hat{V}_c = 124\text{ cm}^3/\text{gmol}$, $z_c = 0.270$.
- *14.3 The critical temperature of a real gas is known to be 500 K, but its critical pressure is unknown. Given that 3 lb mol of the gas at 252°C occupy 50 ft³ at a pressure of 463 psia, estimate the critical pressure.
- *14.4 The volume occupied by 1 lb of n-octane at 27 atm is 0.20 ft³. Calculate the temperature of the n-octane.
- *14.5 A block of dry ice weighing 50 lb was dropped into an empty steel tank, the volume of which is 5.0 ft³. The tank was heated until the pressure gage read 1600 psi. What was the temperature of the gas? Assume all of the CO_2 became gas.
- *14.6 A cylinder containing 10 kg of CH_4 exploded. It had a bursting pressure of 14,000 kPa gauge and a safe operating pressure of 7,000 kPa gauge. The cylinder had an internal volume of 0.0250 m³. Calculate the temperature when the cylinder exploded.
- *14.7 A cylinder has a volume of 1.0 ft³ and contains dry methane at 80°F and 200 psig. What weight of methane (CH_4) is in the cylinder? The barometric pressure is 29.0 m. Hg.
- *14.8 How many kilograms of CO_2 can be put into a 25 liter cylinder at room temperature (25°C) and 200 kPa absolute pressure?
- *14.9 A natural gas composed of 100% methane is to be stored in an underground reservoir at 1000 psia and 120°F. What volume of reservoir is required for 1,000,000 cubic feet of gas measured at 60°F and 14.7 psia?
- *14.10 Calculate the specific volume of propane at a pressure of 6000 kPa and a temperature of 230°C.
- *14.11 State whether or not the following gases can be treated as ideal gases in calculations.
- Nitrogen at 100 kPa and 25°C.
 - Nitrogen at 10,000 kPa and 25°C.
 - Propane at 200 kPa and 25°C.
 - Propane at 2000 kPa and 25°C.

- (e) Water at 100 kPa and 25°C.
 - (f) Water at 1000 kPa and 25°C.
 - (g) Carbon dioxide at 1000 kPa and 0°C.
 - (h) Propane at 400 kPa and 0°C.
- *14.12** One g mol of chlorobenzene (C_6H_5Cl) just fills a tank at 230 kPa and 380 K. What is the volume of the tank?
- **14.13** A size 1A cylinder of ethylene ($T_c = 9.7^\circ C$) costs \$45.92, F.O.B., New Jersey. The outside cylinder dimensions are: 9 in. diameter, 52 in. high. The gas is 99.5% (minimum) C_2H_4 , and the cylinder charge is \$44.00. Cylinder pressure is 1500 psig, and the invoice says it contains 165 cu.ft. of gas. An identical cylinder of CP grade methane at a pressure of 2000 psig is 99.0% (minimum) CH_4 , and costs \$96.00 F.O.B. Illinois. The CH_4 cylinder contains 240 cu. ft. of gas. The ethylene cylinder is supposed to have a gross weight (including cylinder) of 163 lb while the CH_4 cylinder has a gross weight of 145 lb. Answer the following questions:
- (a) What does the "165 cu.ft." and "240 cu.ft." of gas probably mean? Explain with calculations.
 - (b) Why does the CH_4 cylinder have a gross weight less than the C_2H_4 cylinder when it seems to contain more gas? Assume the cylinders are at 80°F.
 - (c) How many pounds of gas are actually in each cylinder?
- **14.14** You have been asked to settle an argument. The argument concerns the maximum allowable working pressure (MWAP) permitted in an A1 gas cylinder. One of your coworkers says that calculating the pressure in a tank via the ideal gas law is best because it gives a conservative (higher) value of the pressure than can actually occur in the tank. The other coworker says that everyone knows the ideal gas law should not be used to calculate real gas pressures as it gives a lower value than the true pressure. Which coworker is correct?
- **14.15** Safe practices in modern laboratories call for placing gas cylinders in hoods or in utility corridors. In case of leaks, a toxic gas can be properly taken care of. A cylinder of CO, that has a volume of 175 ft³ is received from the distributor of gases on Friday with a gauge reading of 2000 psig and is placed in the utility corridor. On Monday when you are ready to use the gas you find the gauge reads 1910 psig. The temperature has remained constant at 76°F as the corridor is air conditioned so you conclude that the tank has leaked CO (which does not smell).
- (a) What has been the leak rate from the tank?
 - (b) If the tank was placed in a utility corridor whose volume is 1600 ft³, what would be the minimum time that it would take for the CO concentration in the hallway to reach the "Ceiling Threshold Limit Value" (TLV-C) of 100 ppm set by the state Air Pollution Control Commission if the air conditioning did not operate on the weekend?
 - (c) In the worst case, what would be the concentration of CO in the corridor if the leak continued from Friday, 3 PM to Monday, 9 AM?
 - (d) Why would not either case (b) or (c) occur in practice?

- *14.16 Levitating solid materials during processing is the best way known to ensure their purity. High-purity materials, which are in great demand in electronics, optics, and other areas, usually are produced by melting a solid. Unfortunately, the containers used to hold the material also tend to contaminate it. And heterogeneous nucleation occurs at the container walls when molten material is cooled. Levitation avoids these problems because the material being processed is not in contact with the container.

Electromagnetic levitation requires that the sample be electrically conductive, but with a levitation method based on buoyancy, the density of the material is the only limiting factor.

Suppose that a gas such as argon is to be compressed at room temperature so that silicon (sp gr 2.0) just floats in the gas. What must the pressure of the argon be? If you wanted to use a lower pressure, what different gas might be selected? Is there a limit to the processing temperature for this manufacturing strategy?

- **14.17 To determine the temperature that occurred in a fire in a warehouse, the arson investigator noticed that the relief valve on a methane storage tank had popped open at 3000 psig, the rated value. Before the fire started, the tank was presumably at ambient conditions, about 80°F, and the gage read 1950 psig. If the volume of the tank was 240 ft³, estimate the temperature during the fire. List any assumptions you make.

- *14.18 When a scuba diver goes to the dive shop to have her scuba tanks filled with air, the tank is connected to a compressor and filled to about 2100 psia while immersed in a tank of water. (Why immerse the tank in water?—So that the compression of air into the tank will be approximately isothermal.)

Suppose that the tank is filled without inserting it into a water bath, and air at 27°C is compressed very rapidly from 1 atm absolute to the same final pressure. The final temperature would be about 700°C. Compute the fractional increase or decrease in the final quantity of air put in the tank relative to the isothermal case assuming that the air behaves as a pure component real gas with $p_c = 37.2$ atm and $T_c = 132.5$ K. Use 0.036 for the Pitzer acentric factor.

- *14.19 A gas is flowing at a rate of 100,000 scfh (standard cubic feet/per hour). What is the actual volumetric gas flow rate if the pressure is 50 atm and the temperature is 600°R? The critical temperature is 40.0°F and the critical pressure is 14.3 atm.

- *14.20 A steel cylinder contains ethylene (C₂H₄) at 200 psig. The cylinder and gas weigh 222 lb. The supplier refills the cylinder with ethylene until the pressure reaches 1000 psig, at which time the cylinder and gas weigh 250 lb. The temperature is constant at 25°C. Calculate the charge to be made for the ethylene if the ethylene is sold at \$0.41 per pound, and what the weight of the cylinder is for use in billing the freight charges. Also find the volume of the empty cylinder in cubic feet.

- *14.21 A gas has the following composition:

CO ₂	10%
CH ₄	40%
C ₂ H ₄	50%

It is desired to distribute 33.6 lb of this gas per cylinder. Cylinders are to be designed so that the maximum pressure will not exceed 2400 psig when the temperature is 180°F. Calculate the volume of the cylinder required by Kay's method.

- *14.22 A gas composed of 20% ethanol and 80% carbon dioxide is at 500 K. What is its pressure if the volume per g mol is 180 cm³/g mol?
- *14.23 A sample of natural gas taken at 3500 kPa absolute and 120°C is separated by chromatography at standard conditions. It was found by calculation that the grams of each component in the gas were:

Component	(g)
Methane (CH ₄)	100
Ethane (C ₂ H ₆)	240
Propane (C ₃ H ₈)	150
Nitrogen (N ₂)	50
Total	540

What was the density of the original gas sample?

- *14.24 A gaseous mixture has the following composition (in mol %):

C ₂ H ₄	57
Ar	40
He	3

at 120 atm pressure and 25°C. Compare the experimental volume of 0.14 L/g mol with that computed by Kay's method.

- *14.25 You are in charge of a pilot plant using an inert atmosphere composed of 60% ethylene (C₂H₄) and 40% argon (A). How big a cylinder (or how many) must be purchased if you are to use 300 ft³ of gas measured at the pilot plant conditions of 100 atm and 300°F. Buy the cheapest array.

Cylinder type	cost	pressure (psig)	lb gas
1A	\$52.30	2000	62
2	42.40	1500	47
3	33.20	1500	35

State any additional assumptions. You can buy only one type of cylinder.

- ✓**14.26 A feed for a reactor has to be prepared comprised of 50% ethylene and 50% nitrogen. One source of gas is a cylinder containing a large amount of gas with the composition 20% ethylene and 80% nitrogen. Another cylinder that contains pure ethylene at 1450 psig and 70°F has an internal volume of 2640 cubic inches. If all the ethylene in the latter cylinder is used up in making the mixture, how much reactor feed was prepared and how much of the 20% ethylene mixture was used?

- ✓**14.27 In a high pressure separations process, a gas having the *mass* composition of 50% benzene, 30% toluene, and 20% xylene is fed into the process at the rate of $483 \text{ m}^3/\text{hr}$ at 607 K and 26.8 atm . One exit stream is a vapor containing 91.2% benzene, 7.2% toluene, and 1.6% xylene. A second exit stream is a liquid containing 6.0% benzene, 9.0% toluene, and 85.0% xylene.

What is the composition of the third exit stream if it is liquid flowing at the rate of $9,800 \text{ kg/hr}$, and the ratio of the benzene to the xylene in the stream is 3 kg benzene to 2 kg xylene?

CHAPTER 15

REAL GASES: EQUATIONS OF STATE

Your objectives in studying this chapter are to be able to:

1. Cite two reasons for using equations of state to predict p - V - T properties of gases.
2. Solve an equation of state given the values of the coefficients in the equation and values of three of the four variables in the set p , V , n , and T .
3. Convert the coefficients in an equation of state from one set of units to another.
4. Find the values of the coefficients for equations of state in the literature on the Internet.

In making calculations with the p - V - T properties of a gas you would like to have good accuracy, reliability, and computational efficiency. In Chapter 14 you learned that the compressibility factor z can be introduced into the ideal gas equation so that the latter can be used to predict properties of real gases. Is there another method to predict physical properties? Read on.

Looking Ahead

In this chapter we describe how equations derived from theory or experiment can be fit from experimental data and used to solve for p , V , n , or T for real gases.

Main Concepts

Although this may seem a paradox, all exact science is dominated by the idea of approximation.

Bertrand Russell

We now describe another way of predicting p , V , n , and T for real gases (either pure components or mixtures), one that differs from the method discussed in Chapter 14, namely by using **equations of state**. The simplest example of an equation of state is the ideal gas law itself. Equations of state can be just empirical relations selected to fit a data set, or they can be based on theory, or a combination of the two. Even if you have experimental data available, in spite of their complications, equations of state are important for several reasons. They permit a concise summary of a large mass of experimental data and also permit accurate interpolation between experimental data points. They provide a continuous function to facilitate calculation of physical properties based on differentiation and integration of p - V - T relationships. Finally, they provide a point of departure for the treatment of the properties of mixtures.

Some of the advantages of using an equation of state versus other prediction methods are:

1. Values of p - V - T can be predicted with reasonable error in regions where no data exist.
2. Only a few values of coefficients are needed in the equation to be able to predict gas properties versus collecting large amounts of data by experiment.
3. The equations can be manipulated on a computer whereas graphics methods cannot.

Some disadvantages are:

1. The form of an equation is hard to change to fit new data.
2. Inconsistencies may exist between equations for p - V - T and equations for other physical properties.
3. Usually the equation is quite complicated and may not be easy to solve for p , V , or T because of its nonlinearity.

I consider that I understand an equation when I can predict the properties of its solutions, without actually solving it.

Paul Dirac

If you plan to use a specific equation of state such as one of those listed in Table 15.1, you have numerous choices, no one of which will consistently give the best results. Examine Mathias and Klotz* and the references therein, consult the references at the end of this chapter, or search the Internet if you want to find a more comprehensive set of equations. You can calculate the values of the coefficients in

*Mathias P.M., and H.C. Klotz. "Take a Closer Look at Thermodynamic Property Models," *Chem. Eng. Progress*, 67-75 (June 1994)

TABLE 15.1 Examples of Equations of State (for 1 g mole)***van der Waals:**

$$\left(p + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT$$

$$a = \left(\frac{27}{64}\right) \frac{R^2 T_c^2}{p_c}$$

$$b = \left(\frac{1}{8}\right) \frac{RT_c}{p_c}$$

Peng-Robinson (PR equation):

$$p = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}(\hat{V} + b) + b(\hat{V} - b)}$$

$$a = 0.45724 \left(\frac{R^2 T_c^2}{p_c} \right)$$

$$b = 0.07780 \left(\frac{RT_c}{p_c} \right)$$

$$\alpha = [1 + \kappa(1 - T_r^{1/2})]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Benedict-Webb-Rubin (BWR equation):

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\sigma}{\hat{V}^2} + \frac{\eta}{\hat{V}^4} + \frac{\omega}{\hat{V}^5}$$

$$\beta = RTB_0 - A_0 - \frac{C^0}{T^2}$$

$$\sigma = bRT - a + \frac{c}{T^2} \exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$\eta = cy \exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$\omega = a\alpha$$

Soave-Redlich-Kwong (SRK equation):

$$p = \frac{RT}{\hat{V} - b} - \frac{a'\lambda}{\hat{V}(\hat{V} + b)}$$

$$a' = \frac{0.42748 R^2 T_c^2}{p_c}$$

$$b = \frac{0.08664 RT_c}{p_c}$$

$$\lambda = [1 + \kappa(1 - T_r^{1/2})]^2$$

$$\kappa = (0.480 + 1.574\omega - 0.176\omega^2)$$

Redlich-Kwong (RK equation):

$$p = \frac{RT}{(\hat{V} - b)} - \frac{a}{T^{1/2}\hat{V}(\hat{V} + b)}$$

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{p_c}$$

$$b = 0.08664 \frac{RT_c}{p_c}$$

Kammerlingh-Onnes (a virial equation):

$$p\hat{V} = RT \left(1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \dots \right)$$

Holborn (a virial equation):

$$p\hat{V} = RT(1 + B'p + C'p^2 + \dots)$$

* T_c and p_c are explained in Chapter 14; \hat{V} is the specific volume; ω is the acentric factor.

several of the equations of state from the critical properties plus the acentric factor of a compound as indicated in Table 15.1. You should note that no adjustable parameters are needed in the van der Waals, Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), and Redlich-Kwong (RK) equations as they are for the virial equations. Because of its accuracy, the data bases in many commercial process simulators make extensive use of the SRK equation of state. These equations in general will not predict p - V - T values across a phase change from gas to liquid very well. Keep in mind that under conditions such that the gas starts to liquefy, the gas laws apply to the vapor phase portion of the system.

How accurate are equations of state? Cubic equations of state such as Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson listed in Table 15.1 can have an accuracy of 1–2% over a large range of conditions for many compounds. Figure 15.1 compares the percent deviation from experimental data of the predicted z using the SRK equation for (a) a polar compound, namely steam, and (b) a light hydrocarbon (C_2H_4), the latter being the gas for which the SRK equation should yield better predictions as it does.

Other classical equations of state are formulated as a power series (called the **virial form**) with p being a function of $1/\hat{V}$ or \hat{V} being a function of p with 3 to 6 terms. Computer databases offer several choices of equations for most compounds. Such relations may be (but may not be) more accurate than cubic equations of state. Equations of state in databases may have as many as 30 or 40 coefficients to achieve high accuracy (see, for example, the AIChE DIPPR reports that can be located on the AIChE web site). Keep in mind you must know the region of validity of any equation of state and not extrapolate outside that region, particularly not into the liquid region!

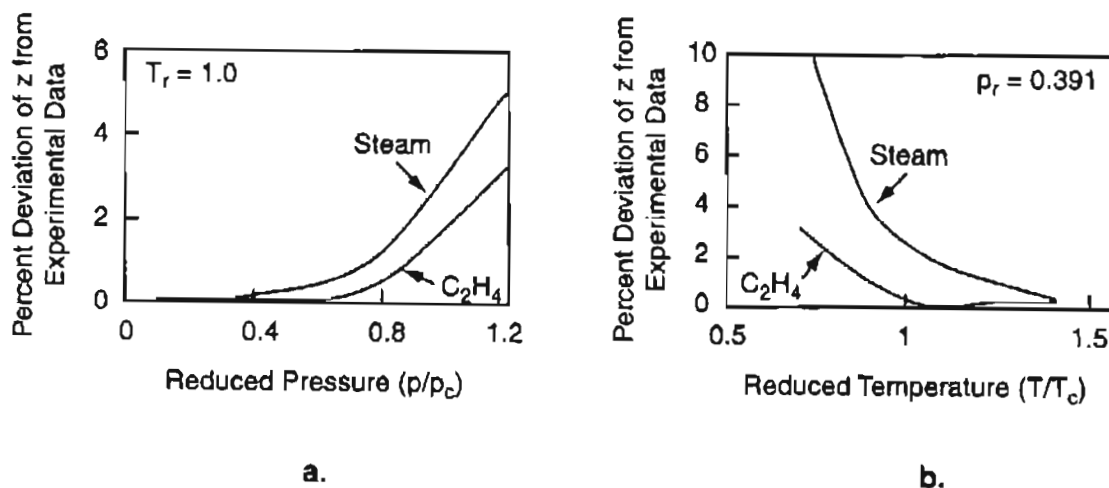


Figure 15.1 Comparison of the percent deviation in the value of z calculated using the SRK equation for a polar compound (steam) and a nonpolar compound (C_2H_4) from the respective experimental values.

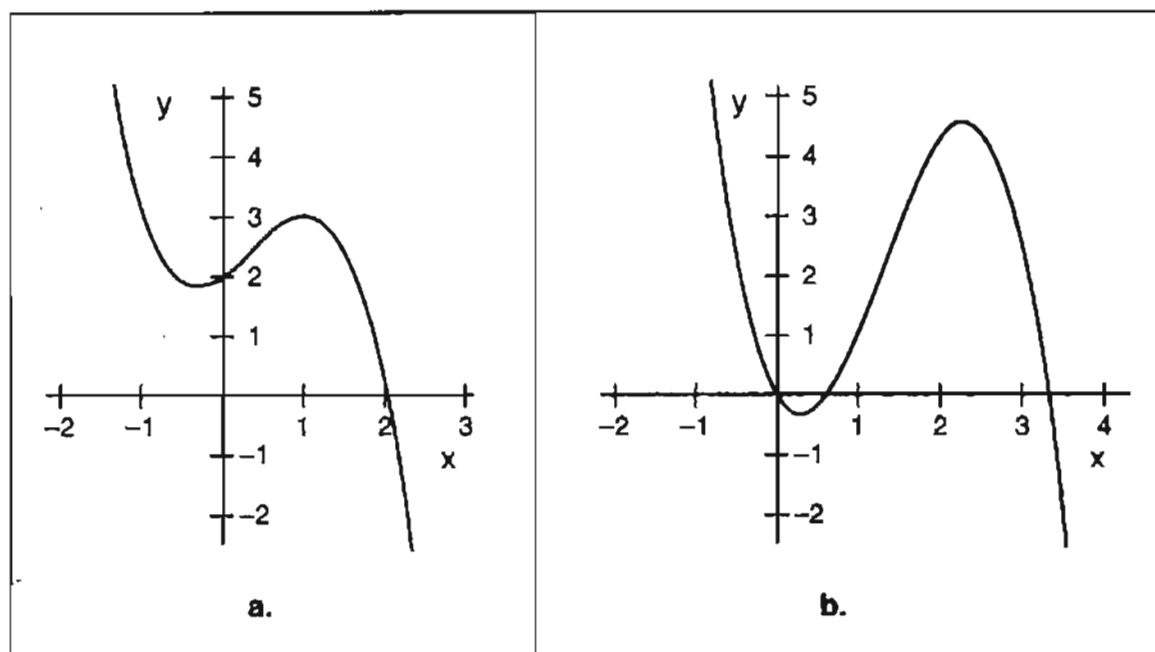


Figure 15.2 Graph (a) shows the existence of one positive real root whereas graph (b) shows the existence of two positive real roots.

One feature of the cubic equations of state listed in Table 15.1 merits comment. In solving for n or V , you must solve a cubic equation that might have more than one real root, as indicated in Figure 15.2.

For example, the van der Waals equation can easily be solved explicitly for p as follows.

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

However, if you want to solve for V (or n), you can see that the equation becomes cubic in V (or n):

$$f(V) = V^3 - \left(nb + \frac{nRT}{p} \right) V^2 + \frac{n^2a}{p} V - \frac{n^3ab}{p} = 0$$

and can have multiple roots (see Figure 15.2). You want a *positive real root* in the gas phase. In Figure 15.2b, the smaller positive root figuratively pertains to the pressure of the liquid. See Pratt* for a good discussion about the meaning of the multiple roots of an equation of state. On the disk that accompanies this book you will find a computer program called Polymath that can solve nonlinear equations, and can be used to solve for V (or n) if you have a *reasonable initial guess* for V (or n), say from

*Pratt, R.M. "Beware of Bogus Roots with Cubic Equations of State," *Chem Eng. Educ.*, 278–281 (Fall 1999).

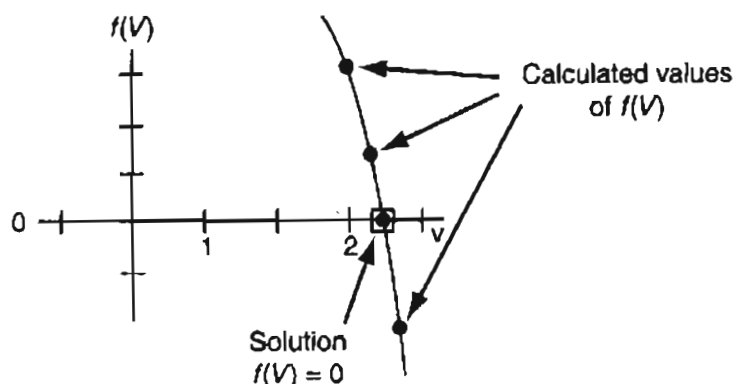


Figure 15.3 Plot of $f(V)$ versus V showing points above and below $f(V) = 0$. The solid line is used in graphical interpolation.

the ideal gas law. Refer to Appendix L2 for the methods of solving nonlinear equations.

An alternative graphical technique for finding the roots of a function of a single variable such as $f(V)$ is to substitute into the function a series of values of V , and find the value of V that causes the value of $f(V)$ to cross the horizontal axis $f(V) = 0$ as V changes. Look at Figure 15.3. You can interpolate for V after bracketing $f(V) = 0$ with values above and below 0.

EXAMPLE 15.1 Application of van der Waals's Equation to Calculate a Temperature

A cylinder 0.150 m^3 in volume containing 22.7 kg of propane C_3H_8 stands in the hot sun. A pressure gauge shows that the pressure is 4790 kPa gauge. What is the temperature of the propane in the cylinder? Use Van der Waals's equation.

Solution

Basis: 22.7 kg of propane

You can obtain the van der Waals constants from any suitable handbook, or by using the critical properties shown in Table 15.1. They are

$$a = 9.24 \times 10^6 \text{ atm} \left(\frac{\text{cm}^3}{\text{g mol}} \right)^2$$

$$b = 90.7 \frac{\text{cm}^3}{\text{g mol}}$$

$$p + \left(\frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

All the additional information you need is as follows:

$$p = \frac{(4790 + 101.3) \text{ kPa}}{101.3 \text{ kPa}} \left| \frac{1 \text{ atm}}{101.3 \text{ kPa}} \right| = 48.3 \text{ atm abs}$$

$$R \text{ in the proper units} = \frac{82.06(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

$$n = \frac{22.7}{44 \text{ kg/kg mol}} = 0.516 \text{ kg mol propane}$$

$$nRT = \left[48.3 + \frac{(0.516 \times 10^3)^2 (9.24 \times 10^6)}{(0.150 \times 10^6)^2} \right] [0.150 \times 10^6$$

$$- (0.516 \times 10^3)(90.7)] = (0.516 \times 10^3)(82.06)(T_K)$$

$$T = 384 \text{ K}$$

Suppose you want to apply the PR or SRK equation in solving the problem posed in Example 15.1. It may not be immediately obvious, but both of these equations require a value for T in order to obtain values for the coefficients in the respective equations, and you do not know T . Look at Table 15.1. Can you locate where T is involved in calculating the values of the coefficients? You might augment the PR or SRK equation with the equation for λ , and solve the pair for T to avoid a trial-and-error solution. Because λ does not change much with temperature, one or two iterations using assumed values of λ should suffice.

EXAMPLE 15.2 Solution of van der Waals's Equation for V

Given the values in a vessel of

$$p = 679.7 \text{ psia} \qquad a = 3.49 \times 10^4 \text{ psia} \left(\frac{\text{ft}^3}{\text{lb mol}} \right)^2$$

$$n = 1.136 \text{ lb mol} \qquad R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})}$$

$$T = 683^\circ\text{R} \qquad b = 1.45 \frac{\text{ft}^3}{\text{lb mol}}$$

solve for the volume of the vessel using Van der Waals's equation.

Solution

Write van der Waals's equation as a cubic equation in one unknown variable, V .

$$f(V) = V^3 - \frac{pnb + nRT}{p}V^2 + \frac{n^2a}{p}V - \frac{n^3ab}{p} = 0 \qquad (\text{a})$$

Let's apply Newton's method (refer to Appendix L2) to obtain the desired root:

$$V_{k+1} = V_k - \frac{f(V_k)}{f'(V_k)} \quad (b)$$

where $f'(V_k)$ is the derivative of $f(V)$ with respect to V evaluated at V_k and the subscript k designates the stage of the calculation

$$f'(V_k) = 3V_k^2 - \frac{2(pnb + nRT)}{p}V_k + \frac{n^2a}{p} \quad (c)$$

In many cases you can obtain a reasonably close approximation to V (or n) from the ideal gas law, useful at least for the first trial in which $k = 0$ in Eq. (b).

$$\begin{aligned} V_0 &= \frac{nRT}{p} = \frac{1.136 \text{ lb mol} \left| \frac{10.73 \text{ (psia)(ft}^3\text{)}}{(\text{lb mol})(^\circ\text{R})} \right| 683^\circ\text{R}}{679.7 \text{ psia}} \\ &= 12.26 \text{ ft}^3 \text{ at } 679.7 \text{ psia and } 683^\circ\text{R} \end{aligned}$$

The second and subsequent estimates of V will be calculated using Equation (b):

$$V_1 = V_0 - \frac{f(V_0)}{f'(V_0)}$$

$$\begin{aligned} f(V_0) &= (12.26)^3 - \frac{(679.7)(1.137)(1.45) + (1.137)(10.73)(683)}{679.7}(12.26)^2 \\ &\quad + \frac{(1.137)^2(3.49 \times 10^4)}{679.7}(12.26) - \frac{(1.137)^2(3.49 \times 10^4)(1.45)}{679.7} = 738.3 \end{aligned}$$

$$\begin{aligned} f'(V_0) &= 3(12.26)^2 - \frac{2[(679.7)(1.137)(1.45) + (1.137)(10.73)(683)]}{679.7}(12.26) \\ &\quad + \frac{(1.137)^2(3.49 \times 10^4)}{679.7} = 216.7 \end{aligned}$$

$$V_1 = 12.26 - \frac{738.3}{216.7} = 8.85$$

On the next iteration

$$V_2 = V_1 - \frac{f(V_1)}{f'(V_1)}$$

and so on until the change in V_k from one iteration to the next is sufficiently small. The Polymath program on the disk in the back of the book will execute this technique for you (and save you considerable time). The final solution is 5.0 ft^3 at 679.7 psia and 683°R .

The **group contribution method** has been successful in estimating p - V - T properties of pure components (as well as other thermodynamic properties). As indicated by the name, the idea is that compounds can be constructed from combinations of functional groups, the contribution of each group to a property can be tabulated, and the group contributions can be correlated and/or summed to give the desired property of the compound. The assumption is that a group such as $-\text{CH}_3$, or $-\text{OH}$, behaves identically no matter what the molecule may be in which it appears. This assumption is not quite true, so that any group contribution method yields approximate values for gas properties. Probably the most widely used group contribution method is UNIFAC,* which forms a part of many computer databases. UNIQUAC is a variant of UNIFAC, and is widely used in the chemical industry in the modeling of nonideal systems (systems with strong interaction between the molecules).

To this point, we have discussed predicting p - V - T properties for *pure* components. How should you treat mixtures of gases? An enormous literature exists describing proposals for *mixing rules*, that is, rules to weight the coefficients for each pure component so that the weighted coefficient can be used in the same equation of state as used for a pure component.

*Even if there is only one possible unified theory it is
just a set of rules and equations*

Stephen Hawking

For example, one set of mixing rules for the Soave-Redlich-Kwong equation suggests to proceed as follows. Let the weighted coefficient (the overlay bar denotes average) be calculated as

$$\overline{a'\lambda} = \sum_{i=1}^n \sum_{j=1}^n y_i y_j (a'\lambda)_{ij}$$

$$\overline{b} = \sum_{i=1}^n y_i b_i$$

where n is the number of components in the mixture, i and j are the indices indicating the pairs of components, y_i is the mole fraction of component i , and $(a'\lambda)_{ij}$ is the product of a' and λ for each of the possible pairs of components. Other simple methods include:

*A. Fredenslund, J. Gmehling, and P. Rasmussen. *Vapor-Liquid Equilibria Using UNIFAC*. Amsterdam: Elsevier, 1977; D. Tiegs, J. Gmehling, P. Rasmussen, and A. Fredenslund. *Ind. Eng. Chem. Res.*, **26**, 159 (1987).

1. Average the coefficients in the equation by the mole fractions of the component gases.
2. Average the results of the solutions of the equations for each gas by the mole fractions of the component gases.
3. Calculate z for each component from the respective equations, and average the z 's.
4. Use coefficients obtained by experiments with mixtures, and interpolate and extrapolate over the desired ranges of variables.

For more information on the topic of mixing rules refer to the references at the end of the chapter.

SELF-ASSESSMENT TEST

Questions

1. Explain why the van der Waals and Peng-Robinson equations (of state) are easy to solve for p and hard to solve for V .
2. Explain some of the problems in obtaining an equation of state $f(p, \hat{V}, T) = 0$ for a gas that is valid for any set of p , \hat{V} , and T .
3. Under what conditions will an equation of state be the most accurate?
4. Will equations of state with many coefficients be more accurate than equations of state that involve only two or three coefficients?
5. How can you get values for the coefficients in equations of state given the experimental data for p , V , and T ?
6. How can you convert any of the equations of state that are explicit in p to a form explicit in z ?
7. What are the units of a and b in the SI system for the Redlich-Kwong equation?

Problems

1. Convert the virial (power series) equations of Kammerlingh-Onnes and Holborn (in Table 15.1) to a form that yields an expression for z .
2. Repeat for the Van der Waals and Peng-Robinson equations.
3. For the Peng-Robinson equation of state, plot p (in MPa) on an arithmetic scale versus \hat{V} (in m^3/kg) on a \log_{10} scale showing data and the corresponding predicted values of $p - \hat{V}$ for a compound. Use $T_r = 1.1$, $T_r = 0.85$, and $T_r = 0.73$ as the temperature isotherms for the predictions and the data.
4. Predict \hat{V} for CO_2 at 310K and 7500 kPa using the (a) ideal gas law, (b) generalized z charts, (c) Holborn equation ($B' = -0.00851 \text{ atm}^{-1}$ and $C' = 2.40 \times 10^{-5} \text{ atm}^{-2}$),

and (d) van der Waals equation. The Pitzer relation gives $z = 0.514$. The experimental value is $\hat{V} = 3.90 \text{ cm}^3/\text{g}$.

5. You measure that 0.00220 lb mol of a certain gas occupies a volume of 0.95 ft³ at 1 atm and 32°F. If the equation of state for this gas is $pV = nRT(1 + bp)$, where b is a constant, find the volume at 2 atm and 71°F.
6. Calculate the temperature of 2 g mol of a gas using van der Waals's equation with $a = 1.35 \times 10^{-6} (\text{m}^6)(\text{atm})(\text{g mol}^{-2})$, $b = 0.0322 \times 10^{-3} (\text{m}^3)(\text{g mol}^{-1})$ if the pressure is 100 kPa and the volume is 0.0515 m³.
7. Calculate the pressure of 10 kg mol of ethane in a 4.86 m³ vessel at 300 K using two equations of state: (a) ideal gas and (b) Soave-Redlich-Kwong. Compare your answer with the observed value of 34.0 atm.
8. The van der Waals constants for a gas are $a = 2.31 \times 10^6 (\text{atm})(\text{cm}^3)/(\text{g mol})^2$ and $b = 44.9 \text{ cm}^3/\text{g mol}$. Find the volume per kilogram mole if the gas is at 90 atm and 373 K.

Thought Problems

1. Data pertaining to the atmosphere on Venus (which has a gravitational field only 0.81 of that of the Earth) shows that the temperature of the atmosphere at the surface is $474 \pm 20^\circ\text{C}$ and the pressure is $90 \pm 15 \text{ atm}$. What do you think is the reason(s) for the difference between these figures and those at the Earth's surface?
2. A method of making protein nanoparticles (0.5 to 5.0 μm in size) has been patented by the Aphio Corp. Anti-cancer drugs that small can be used in novel drug delivery systems. In the process described in the patent, protein is mixed with a gas such as carbon dioxide or nitrogen at ambient temperature and 20,000 kPa pressure. When the pressure is released, the proteins break up into fine particles.

What are some of the advantages of such a process versus making powders by standard methods?

Discussion Problems

1. Fossil fuels provide most of our power, and the carbon dioxide produced is usually discharged to the atmosphere. The Norwegian company Statoil separates carbon dioxide from its North Sea gas production, and, since 1996, has been pumping it at the rate of 1 million tons per year into a layer of sandstone 1 km below the seabed. The sandstone traps the gas in a gigantic bubble that in 2001 contained 4 million tons of carbon dioxide.
Will the bubble of carbon dioxide remain in place? What problems exist with regard to the continuous addition of carbon dioxide in future years? Is the carbon dioxide actually a gas?
2. What are some of the tests you might apply to determine if an equation of state fits p - V - T data?
3. What factors in a real gas cause the gas to behave in a nonideal manner? Are these factors taken into account in the equations of state listed in Table 15.1?

Looking Back

We provided a condensed view of equations of state for pure components in this chapter, citing their advantages and disadvantages, expected accuracy, and examples of application. We also mentioned briefly one way to treat gas mixtures.

GLOSSARY OF NEW WORDS

Benedict-Webb-Rubin An eight-parameter equation of state that relates the physical properties p , V , T , and n for a gas.

Group contribution method A technique of estimating physical properties of compounds by using properties of molecular groups of elements in the compound.

Holborn A multiple parameter equation of state expanded in p .

Kammerlingh-Onnes A multiple parameter equation of state expanded in V^{-1} .

Peng-Robinson A three-parameter equation of state.

Soave-Redlich-Kwong A three-parameter equation of state.

UNIFAC A group contribution method of estimating physical properties.

UNIQUAC An extension of the UNIFAC method of estimating physical properties.

Van der Waals A two-parameter equation of state.

Virial equation of state An equation of state expanded in successive terms of one of the physical properties.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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<http://che201.vu.msu.edu/701/topic07/lesson11/111p05.htm>
<http://www.che.ufl.edu/courses/ECH3023/lectures/acomplex/acomplex.html>
<http://flory.engr.utk.edu/che330/L6-1.gif>
<http://forums.mit.edu/acad?13@104.jaYQFqd1^20@.ee6cfl4>
www.virtualmaterials.com/cep2001.html

PROBLEMS

- *15.1 You want to obtain an answer immediately as to the specific volume of ethane at 700 kPa and 25°C. List in descending order the techniques you would use with the most preferable one at the top of the list:
- (a) Ideal gas law
 - (b) Compressibility charts
 - (c) An equation of state

- (d) Look up the value on the web
- (e) Look up the value in a handbook

Explain your choices.

- *15.2** Which procedure would you recommend to calculate the density of carbon dioxide at 120°F and 1500 psia? Explain your choice.
- (a) Ideal gas law
 - (b) Redlich-Kwong equation of state
 - (c) Compressibility charts
 - (d) Look up value on the web
 - (e) Look up value in a handbook
- *15.3** Finish the following sentence:
Equations of state are preferred in PVT calculations because
- *15.4** Use the Kammerlingh-Onnes virial equation with four terms to answer the following questions for CH₄ at 273 K:
- (a) Up to what pressure is one term (the ideal gas law) a good approximation?
 - (b) Up to what pressure is the equation truncated to two terms a good approximation?
 - (c) What is the error in using (a) and using (b) for CH₄?

Data: At 273K the values of the virial coefficients are:

$$\begin{aligned} B &= -53.4 \text{ cm}^3/\text{mol} \\ C &= 2,620 \text{ cm}^6/\text{mol}^{-2} \\ D &= 5000 \text{ cm}^9/\text{mol}^{-3} \end{aligned}$$

- **15.5** You are asked to design a steel tank in which CO₂ will be stored at 290K. The tank is 10.4 m³ in volume and you want to store 460 kg of CO₂ in it. What pressure will the CO₂ exert? Use the Redlich-Kwong equation to calculate the pressure in the tank. Repeat using the SRK equation. Is there a significant difference in the predictions of pressure between the equations?
- *15.6** The Peng-Robinson equation is listed in Table 15.1. What are the units of a , b , and α in the equation if p is in atm, \hat{V} is in L/g mol, and T is in K?
- *15.7** The pressure gauge on an O₂ cylinder stored outside at 0°F in the winter reads 1375 psia. By weighing the cylinder (whose volume is 6.70 ft³) you find the net weight, that is, the O₂, is 63.9 lb. Is the reading on the pressure gauge correct? Use an equation of state to make your calculations.
- ✓ *****15.8** What pressure would be developed if 100 ft³ of ammonia at 20 atm and 400°F were compressed into a volume of 5.0 ft³ at 350°F? Use the Peng-Robinson equation to get your answer.
- **15.9** An interesting patent (U.S. 3,718,236) explains how to use CO₂ as the driving gas for aerosol sprays in a can. A plastic pouch is filled with small compartments containing sodium bicarbonate tablets. Citric acid solution is placed in the bottom of the pouch, and a small amount of carbon dioxide is charged under pressure into the pouch as a starter propellant. As the product is CO₂ dispensed, the carbon dioxide expands, rupturing the lowest compartment membrane, thus dropping bicarb tablets into the citric

acid. That generates more carbon dioxide, giving more pressure in the pouch, which expands and helps push out more product. (The CO_2 does not escape from the can, just the product.)

How many grams of NaHCO_3 are needed to generate a residual pressure of 81.0 psig in the can to deliver the very last cm^3 of product if the cylindrical can is 8.10 cm in diameter and 17.0 cm high? Assume the temperature is 25°C . Use the Peng-Robinson equation.

- ***15.10** First commercialized in the 1970s as extractants in “natural” decaffeination processes, SCFs (supercritical fluids)—particularly carbon dioxide and water—are finding new applications, as better, less-expensive equipment lowers processing costs, and regulations drive the chemical process industries away from organic solvents.

SCFs’ extraction capabilities are now being exploited in a range of new pharmaceutical and environmental applications, while supercritical extraction, oxidation and precipitation are being applied to waste cleanup challenges.

A compressor for the carbon dioxide compresses $2,000 \text{ m}^3/\text{min}$ at 20°C and 500 kPa to 110°C and 4800 kPa. How many m^3/min are produced at the high pressure. Use Van der Waals’ equation.

- **15.11** A 5-L tank of H_2 is left out overnight in Antarctica. You are asked to determine how many g moles of H_2 are in the tank. The pressure gauge reads 39 atm gauge and the temperature is -50°C . How many g moles of H_2 are in the tank?

Use the van der Waals and Redlich-Kwong equations of state to solve this problem. (*Hint:* The nonlinear-equation-solving program on the CD in the pocket at the back of this book will make the execution of the calculations quite easy.)

- **15.12** Find the molar volume (in $\text{cm}^3/\text{g mol}$) of propane at 375 K and 21 atm. Use the Redlich-Kwong and Peng-Robinson equations, and solve for the molar volume using the nonlinear equation solver on the CD in the pocket at the back of this book. The acentric factor for propane to use in the Peng-Robinson equation is 0.1487.

- **15.13** 4.00 g mol of CO_2 is contained in a 6250-cm^3 vessel at 298.15 K and 14.5 atm. Use the nonlinear equation solver on the CD in the back of the book to solve the Redlich-Kwong equation for the molar volume. Compare the calculated molar volume of the CO_2 in the vessel with the experimental value.

- **15.14** The tank cited in problem 15.5 is constructed and tested, and your boss informs you that you forgot to add a safety factor in the design of the tank. It tests out satisfactorily to 3500 kPa, but you should have added a safety factor of 3 to the design, that is, the tank pressure should not exceed $(3500/3) = 1167 \text{ kPa}$, say 1200 kPa. How many kg of CO_2 can be stored in the tank if the safety factor is applied? Use the Redlich-Kwong equation. *Hint:* Polymath will solve the equation for you.

- **15.15** A graduate student wants to use van der Waals’ equation to express the pressure-volume-temperature relations for a gas. Her project required a reasonable degree of precision in the p - V - T calculations. Therefore, she made the following experimental measurements with her setup to get an idea of how easy the experiment would be:

Temperature, K	Pressure, Atm	Volume, ft ³ /lb mol
273.1	200	1.860
273.1	1000	0.741

Determine values for the values of constants a and b to be used in van der Waals' equation that best fit the experimental data.

- **15.16** An 80-lb block of ice is put into a 10-ft³ container, and heated to 900K. What is the final pressure in the container. Do this problem two ways: (1) use the compressibility factor method, and (2) use the Redlich-Kwong equation. Compare your results.
- **15.17** What weight of ethane is contained in a gas cylinder that is 1.0-ft³ in volume if the gas is at 100°F and 2000 psig? Do this problem two ways: (1) use Van der Waals' equation, and (2) use the compressibility factor method. The experimental value is 21.4 lb.
- *15.18** Answer the following questions:
- Will the constant a in van der Waals' equation be higher or lower for methane than for propane? Repeat for the other Van der Waals constant b .
 - Will the constant a' in the SRK equation be higher or lower for methane than for propane? Repeat for the other van der Waals constant b .
- **15.19** Oxygen at -18°C is taken from a tank at a rate of 0.190 m³/hr, and mixed with ethane to be fed to an engine along with 100% excess air. The exhaust from the engine is 2593 m³ measured at standard conditions per hour, and has the following composition:

Component	Percent
O ₂	9.89
N ₂	74.41
CO ₂	5.65
CO	0.63
H ₂ O	9.42

What is the pressure in the tank from which the oxygen is being withdrawn?

- **15.20** A feed for a reactor has to be prepared comprised of 50% ethylene and 50% nitrogen. One source of gas is a cylinder containing a large amount of gas with the composition 20% ethylene and 80% nitrogen. Another cylinder that contains pure ethylene at 1450 psig and 70°F has an internal volume of 2640 cubic inches. If all the ethylene in the latter cylinder is used up in making the mixture, how much reactor feed was prepared and how much of the 20% ethylene mixture was used? Use van der Waals' equation and compare your answers with those obtained in Problem 14.26.

CHAPTER 16

SINGLE-COMPONENT TWO-PHASE SYSTEMS (VAPOR PRESSURE)

16.1 Phase Diagrams

476

16.2 Modeling and Predicting Vapor Pressure as a Function of Temperature

485

***Your objectives in studying this
chapter are to be able to:***

1. Define and explain several important terms related to the properties of water that are listed in Section 16.1.
2. Sketch the vapor pressure of a pure compound as a function of temperature at constant volume and a function of volume at constant temperature.
3. Sketch the processes of vaporization, condensation, compression, and expansion of a pure compound on p^* versus T and p^* versus \hat{V} charts.
4. Explain what occurs in terms of p^* , \hat{V} , and T during a phase transition.
5. Calculate the vapor pressure of a substance from an equation that relates the vapor pressure to the temperature (such as the Antoine equation) given values for the coefficients in the equation.
6. Look up the vapor pressure in reference books.
7. Calculate the temperature of a substance from a vapor-pressure equation given the values for the coefficients in the equation and the vapor pressure.
8. Estimate the vapor pressure of a compound via a Cox chart.
9. Use the steam tables to retrieve data for the vapor pressure of water.

When you read subsequent chapters you will need to be quite clear as to how to obtain vapor pressure data and use it in your calculations. Now is your opportunity to familiarize yourself with the pertinent graphs, equations, and tables so that you will avoid confusion later on.

Looking Ahead

In this chapter we want to add a number of new terms to your vocabulary related to liquids and vapors. In addition, we describe some useful types of phase diagrams. Then we proceed to discuss the prediction of vapor pressure as a function of temperature, and introduce you to the steam tables in which you can look up the vapor pressure of water.

16.1 Phase Diagrams

You can conveniently display the properties of compounds via **phase diagrams**. A pure substance can exist simultaneously in many phases, of which, as you know, solid, liquid, and gas are the most common.

Phase diagrams enable you to view the properties of two or more phases as functions of temperature, pressure, specific volume, concentration, and other variables. Tables and equations may yield greater accuracy, but “a picture is worth a thousand words” or in our case, a thousand bits of data.

We are going to discuss phase diagrams in terms of water because presumably you are familiar with the three phases of water, namely ice, liquid water, and water vapor (steam), but the discussion applies to all other pure substances. The terms *vapor* and *gas* are used very loosely. A gas that exists below its critical temperature is usually called a vapor because it can condense. We will reserve the word **vapor** to describe a gas below its critical point in a process in which the phase change is of primary interest, while the word **gas** or **noncondensable gas** will be used to describe a gas above the critical point or a gas in a process at conditions under which it cannot condense.

Suppose you carry out some experiments with the apparatus shown in Figure 16.1. Place a lump of ice in the chamber below the piston, and evacuate the chamber to remove all of the air (you want to retain only pure water in the chamber). Fix the volume of the chamber by fixing the position of the piston, and start slowly (so that the phases of water that result will be in equilibrium) heating the ice. If you plot the measured pressures as a function of temperature, you will get Figure 16.2—a phase diagram—in which all of the measurements you make have been fitted by a continuous smooth curve for clarity.

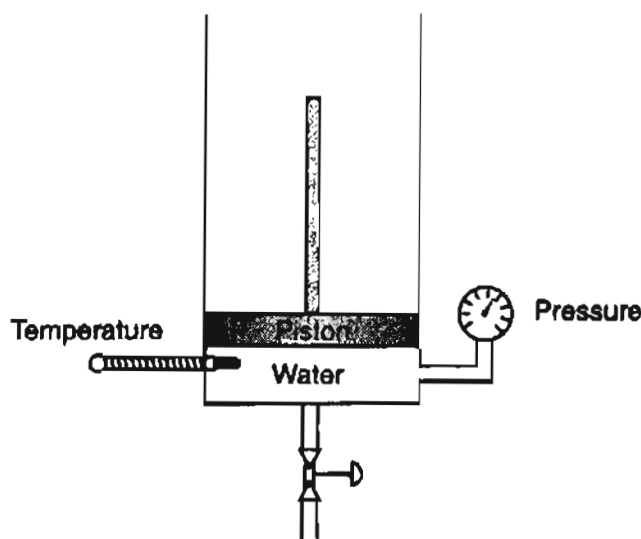


Figure 16.1 Apparatus used to explore the p , \hat{V} , and T properties of water.

The initial conditions of p and T in the chamber are at O in Figure 16.2 with the solid in equilibrium with the vapor.

As you raise the temperature the ice starts to melt at point A, the **triple point**, the one p - T - \hat{V} combination at which solid, liquid, and vapor can be in equilibrium. Further increases in the temperature cause the pressure to rise along the curve AB that represents liquid and vapor in equilibrium. B is the critical point at which vapor and liquid properties become the same.

At point A, if you had kept the temperature constant and raised the pressure on the ice, ice would still exist and be in equilibrium with liquid water along the line AC (C is not the termination of the line, just a marker for convenience in descrip-

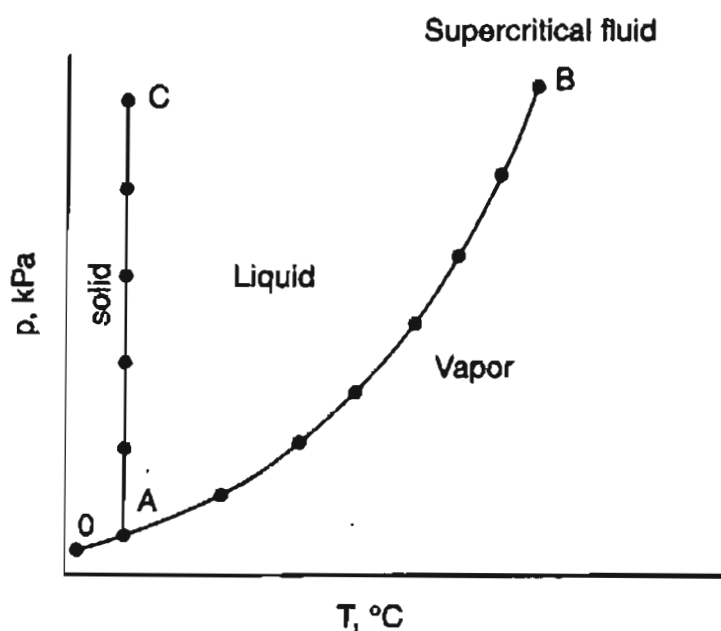


Figure 16.2 Results of an experiment in heating a fixed amount of a pure compound in a closed vessel (a constant volume) as shown on a phase diagram of p versus T at constant \hat{V} .

tion). The line AC is so vertical that *you can use the saturated liquid properties for the compressed liquid*. For example, saturated water at 400K and $p^* = 245.6$ kPa has a density of 937.35 kg/m^3 . If the pressure on the water is increased at 400K to 1000 kPa, the density is 937.79 kg/m^3 , an increase of just 0.047%. Ice skating is possible because the high pressure exerted by the thin blade on ice forms a liquid layer with low friction on the blade. Skis usually do not exert enough pressure to melt the snow, in fact skis are frequently waxed to reduce friction.

If the vapor and liquid of a pure component are in **equilibrium**, then the **equilibrium pressure is called the vapor pressure**, which we will denote by p^* . **At a given temperature there is only one pressure at which the liquid and vapor phases of a pure substance may exist in equilibrium.** Either phase alone may exist, of course, over a wide range of conditions.

We next take up some terminology associated with processes that are conveniently represented on a p^*-T phase diagram such as Figure 16.3 (the letters in parenthesis refer to a process shown in Figure 16.3). You will note that some of the states or processes, for historical reasons, have duplicate names.

boiling

The change of phase from liquid to vapor (e.g., D to F, A to C, or M to O).

bubble point

The temperature at which a liquid just starts to vaporize (N, H, and E are examples).

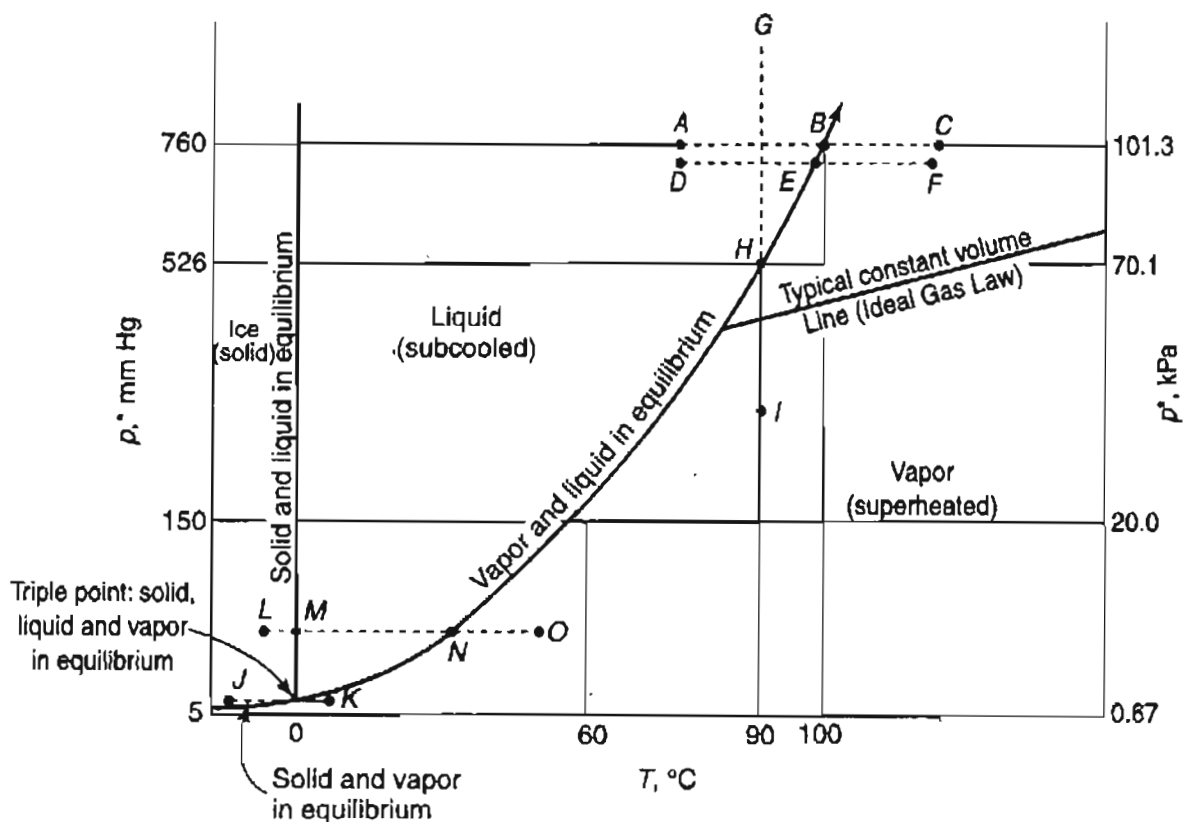


Figure 16.3 Various common processes as represented on a p^*-T diagram.

condensation	The change of phase from vapor to liquid (e.g., F to D, C to A, or O to M).
dew point	The temperature at which the vapor just begins to condense at a specified pressure, namely temperature values along the vapor pressure curve (N, H, and E are examples).
evaporation	The change of phase from liquid to vapor (e.g., D to F, A to C, or M to O).
freezing (solidifying)	The change of phase from liquid to solid (N to L).
melting (fusion)	The change in phase from solid to liquid (L to M).
melting curve	The solid–liquid equilibrium curve starting at the triple point and continuing vertically through M.
normal boiling point	The temperature at which the vapor pressure (p^*) is 1 atm (101.3 kPa)—point B for water.
normal melting point	The temperature at which the solid melts at 1 atm (101.3 kPa).
saturated liquid/saturated vapor	Values along the liquid and vapor equilibrium curve (vapor pressure curve).
subcooled liquid	Liquid between the melting curve and the vapor pressure curve (D is an example).
sublimation	The change in phase from solid to vapor (J to K).
sublimation curve	The solid–vapor equilibrium curve from J (and lower) to the triple point.
sublimation pressure	The pressure along the sublimation curve (a function of temperature)
supercritical region	p - T values for liquid and vapor (“fluid”) above the critical point.
superheated vapor	Vapor at temperatures and pressures exceeding those at saturation (I is an example). The degrees of superheat are the difference (O minus N or F minus E) in temperature between the actual T and the saturated T at the given pressure. For example, steam at 500°F and 100 psia (the saturation temperature for 100 psia is 327.8°F) has $(500 - 327.8) = 172.2^\circ\text{F}$ of superheat.

two-phase region

Conditions of T and p in which two phases can coexist at equilibrium (the region comprising the vapor and liquid is compressed into the curve N-H-E-B in Figure 16.3)

vaporization

The change of phase from liquid to vapor, that is, boiling (D to F).

In Figure 16.3 the process of evaporation and condensation of water at 1 atm is represented by the line ABC with the phase transformation occurring at 100°C. Suppose that you went to the top of Pikes Peak and repeated the process of evaporation and condensation in the open air. What would happen then? The process would be the same (points *D-E-F*) with the exception of the temperature at which the water would begin to boil, or condense. Since the pressure of the atmosphere at the top of Pikes Peak is lower than 101.3 kPa, the water would start to displace the air, or boil, at a lower temperature. Some unfortunate consequences might result if you expected to kill certain types of disease-causing bacteria by boiling!

To conclude, you can see that (a) at any given temperature water exerts its vapor pressure (at equilibrium); (b) as the temperature increases, the vapor pressure increases as well; and (c) it makes no difference whether water vaporizes into air, into a cylinder closed by a piston, or into an evacuated cylinder—at any temperature it still exerts the same vapor pressure as long as the liquid water is in equilibrium with its vapor.

A pure compound can change at constant volume from a liquid to a vapor, or the reverse, via a constant temperature process as well as a constant pressure process. A process of **vaporization** or **condensation at constant temperature** is illustrated by the lines *G-H-I* or *I-H-G*, respectively, in Figure 16.3. Water would vaporize or condense at constant temperature as the pressure reaches point *H* on the vapor-pressure curve. The change that occurs at *H* is the increase or decrease in the fraction of vapor or liquid, respectively, at the fixed temperature. The pressure does not change until all of the vapor, or liquid, has completed the phase transition.

Now let's go back to the experimental apparatus and collect data to prepare a graph of the values of p and \hat{V} as a function of temperature. This time you want to hold the temperature in the chamber constant and adjust the volume while measuring the pressure. Start with compressed liquid water (subcooled water) rather than ice, and raise the piston so that water eventually vaporizes as the pressure drops. Figure 16.4 illustrates by dashed lines the measurements for two different temperatures, T_1 and T_2 . As the pressure is reduced at constant T_1 , \hat{V} increases very slightly (liquids are not very compressible) until the liquid pressure reaches p^* , the vapor pressure, at point A.

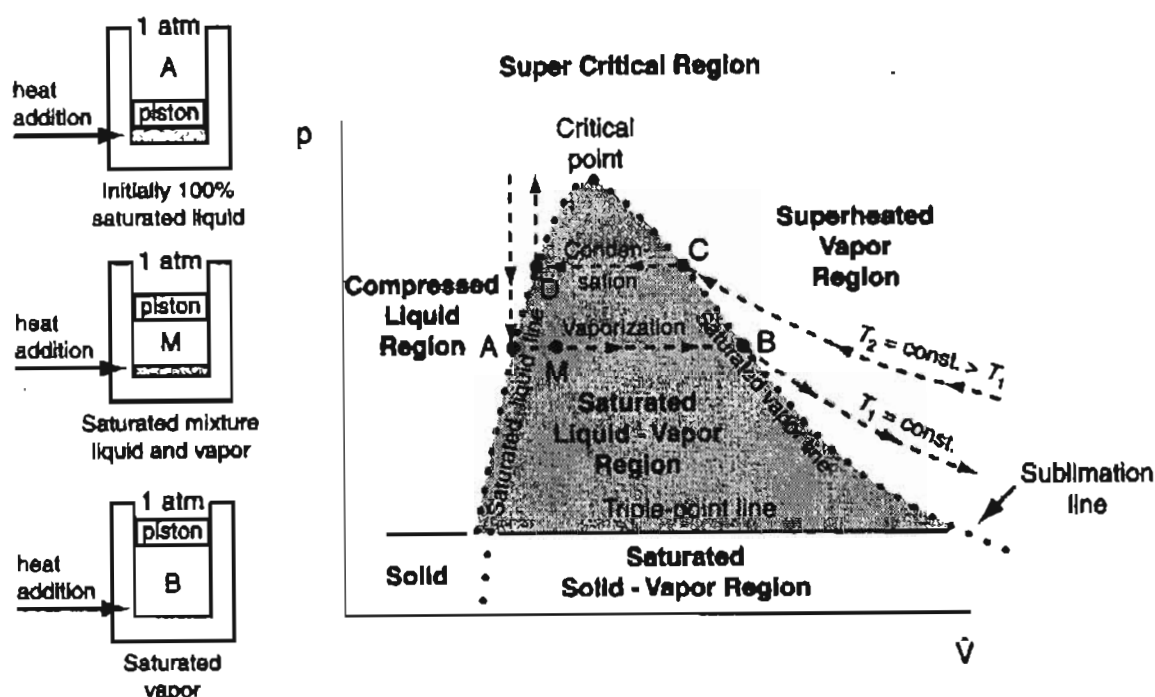


Figure 16.4 Experiments to obtain a p - \hat{V} phase diagram. The dashed lines are measurements made at constant temperatures T_1 and T_2 . The dots represent the points at which vaporization or condensation, respectively, of the saturated liquid, or vapor, occurs, and form an envelope about the two-phase region.

Then, as the piston continues to rise, both the pressure and temperature remain constant as the liquid vaporizes until all of the liquid is vaporized (point B) on the saturated vapor line.

Subsequently, as the pressure decreases, the value of \hat{V} can be calculated via an ideal or real gas equation. Compression at constant T_2 is just a reversal of the process at T_1 . The dots in Figure 16.4 represent just the measurements made when saturation of liquid and vapor occurs, and are deemed to form the envelope for the **two-phase** region that from a different perspective appears in Figures 16.2 and 16.3 as the vapor pressure curve. The two-phase region (e.g., A to B or D to C in Figure 16.4) represents the conditions under which liquid and vapor can exist at equilibrium. Note from Figure 16.4 that a change in the specific volume occurs in going from a liquid to a solid at the triple point. In other words, water expands when it freezes and this is why ships trapped in the polar ice can be crushed by the force of the expanding ice.

A new term, **quality**, the fraction or percent of the total vapor and liquid mixture that is vapor (wet vapor), applies to the two-phase region. Examine Figure 16.5.

You can calculate the volume of the liquid-vapor mixture at B in Figure 16.5 by adding the volume fraction of material that is saturated liquid to the volume fraction that is saturated vapor

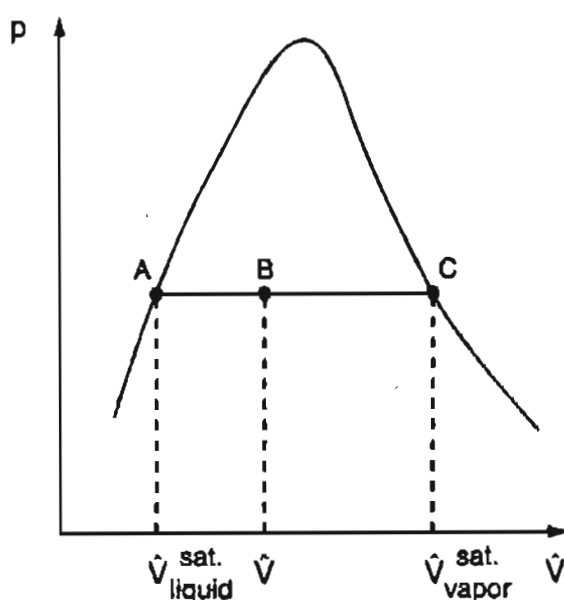


Figure 16.5 Representation of quality on a p - \hat{V} phase diagram. A is saturated liquid and C is saturated vapor. The compound at B is part liquid and part vapor, and the fraction vapor is called the quality.

$$\hat{V} = (1 - x)\hat{V}_{\text{saturated liquid}} + x\hat{V}_{\text{saturated vapor}} \quad (16.1)$$

where x is the fractional quality. Solving for x yields

$$x = \frac{\hat{V} - \hat{V}_{\text{liquid}}^{\text{sat.}}}{\hat{V}_{\text{vapor}}^{\text{sat.}} - \hat{V}_{\text{liquid}}^{\text{sat.}}}$$

Graphs of physical properties frequently display lines of constant quality in the two-phase region. Examine Figure J2 for CO_2 in Appendix J.

Figures 16.3 and 16.4 can be reconciled by looking at the three-dimensional surface that illustrates the p - \hat{V} - T functionality for water, Figure 16.6.

You can see that the vapor pressure curve shown in Figures 16.2 and 16.3 corresponds to a two-dimensional projection of a three-dimensional surface onto the p - T plane. The view you see is directly across the surface representing the liquid-vapor region. A slight expansion of the projection in the lower left shows more detail. For each temperature you can read the corresponding pressure at which water vapor and liquid water exist in equilibrium. Similarly, the p - \hat{V} projection corresponds to a view you would have looking across the three-dimensional surface standing in front of the specific volume axis.

Frequently Asked Questions

1. Does saturation really refer both to the liquid and to the vapor? Yes, both can be termed saturated.
2. Does the dew point mean the same thing as saturated? Yes, for saturated vapor.
3. Does the bubble point mean the same thing as saturated? Yes, for saturated liquid.

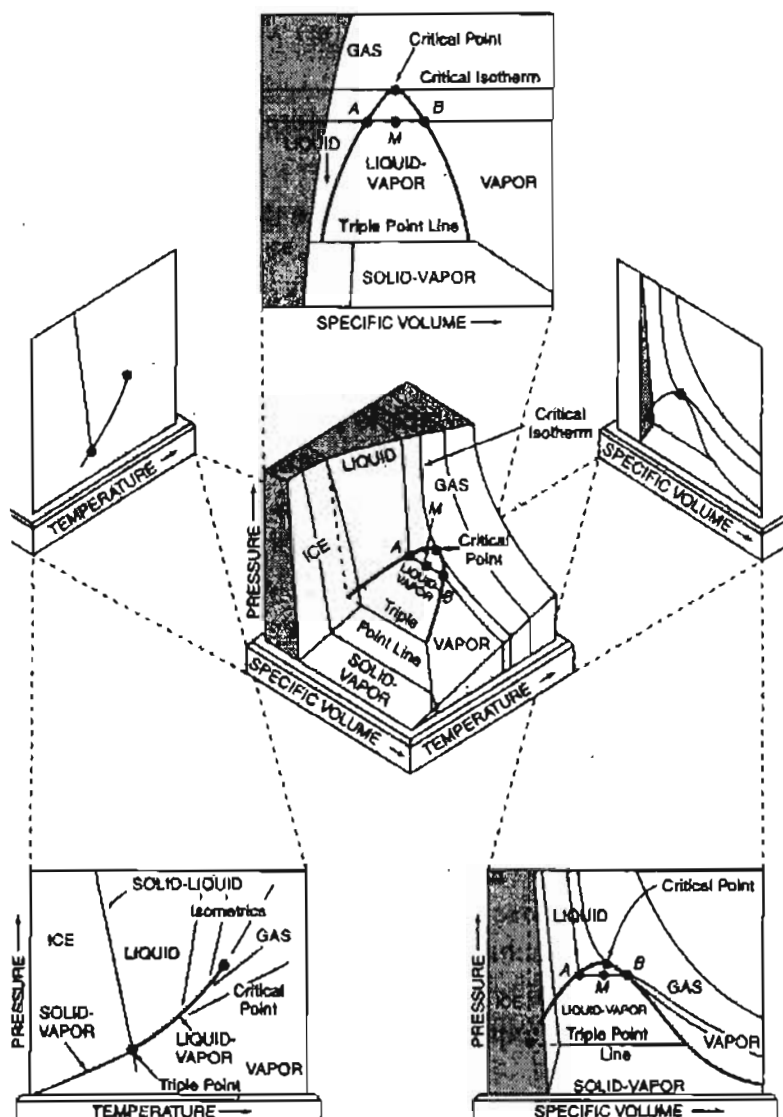


Figure 16.6 The p - \hat{V} - T surface for water (a compound that expands on freezing) showing the two-dimensional projections for pairs of the three variables.

4. Is the saturation pressure really the same thing as the vapor pressure? Yes.
5. Why can you use some of the properties of saturated liquid for liquid at higher pressures than saturation? Inspection of a p - V diagram shows that the phase boundary (line) between the liquid and vapor is essentially a vertical line. Consequently, the specific volume, e.g., the density, of the liquid remains essentially unchanged as the pressure increases.

SELF-ASSESSMENT TEST

Questions

1. If CuSO_4 (a solid) is heated to 653°C it begins to decompose to CuO , SO_2 , and O_2 . An article shows a plot of the partial pressure of SO_2 versus temperature with the caption stating "Vapor pressure of copper sulfate as a function of temperature." Do you think the caption is correct?
2. You wish to produce solid nitrous oxide using the same equipment and process as used for solid carbon dioxide. Where would you locate your plant—at low or high altitude?

How would you ship your product to a distant point (say, Houston) where the solid N_2O is to be liquified and bottled? How would you liquify the solid?

3. Does iodine have a vapor pressure? Does it melt at room temperature?
4. Why does dry ice sublime at room temperature and pressure?
5. Is it true that foods cook more quickly in a pressure cooker because the temperature inside the cooker is higher than the temperature obtained in an open pot?

Problems

1. A tank contains 1000 kg of acetone ($\text{C}_3\text{H}_6\text{O}$), half of which is liquid and the other half is the vapor phase. Acetone vapor is withdrawn slowly from the tank, and a heater in each phase maintains the temperature of each of the two phases at 50°C . Determine the pressure in the tank after 100 kg of vapor has been withdrawn.
2. Draw a p - T phase diagram for water. Label the following clearly: vapor-pressure curve, dewpoint curve, saturated region, superheated region, subcooled region, and triple point. Show the processes of evaporation, condensation, and sublimation by arrows.

Thought Problems

1. A cylinder containing butadiene exploded in a research laboratory, killing one employee. The cylinder had been used to supply butadiene to a pilot plant. When butadiene gas was required, heat was supplied to the cylinder to raise the pressure of the butadiene in the tank. The maximum temperature that could be achieved in the tank on subsequent tests with a like tank was 160°C . At 152°C , the critical temperature for butadiene, the pressure is 628 lb/in.^2 , less than one-half of the pressure required to rupture the tank by hydraulic test. Why did the tank explode?
2. The advertisement reads "Solid dry ice blocks in 60 seconds right in your own lab! Now you can have dry ice available to you at any time, day or night, with this small, safe, efficient machine and readily available CO_2 cylinders. No batteries or electrical energy are required." How is it possible to make dry ice in 60 seconds without a compressor?
3. An inventor is trying to sell a machine that transforms water vapor into liquid water without ever condensing the water vapor. You are asked to explain if such a process is technically possible. What is your answer?

Discussion Problems

1. The following description of a waste disposal system appeared in *Chemical Engineering*, June 1993, p. 23.

The first commercial application of VerTech Deep Shaft, a wet oxidation process that takes place in a reactor suspended in a borehole about 1,250 m deep, has been commissioned to treat 25,000 m.t./yr of sewage sludge at a municipal wastewater treatment plant in Apeldoorn, The Netherlands. The reactor consists of three steel tubes suspended in a 1,250-m drilled shaft of 95 cm dia. A 5% sludge solution is pumped down the inner 19.5-cm-dia. open-ended tube, while the oxidized sludge

and dissolved gases come up through the annular space between the first tube and the closed second tube (34 cm dia.). About 400 m down, pure oxygen is sparged into the sludge to promote oxidation of the suspended organic matter. The static head of the 1,200-m column prevents boiling at about 280°C and 100 bars. The alternatives: incineration, composting, drying, or conventional wet oxidation have per m.t. costs of DGL 790, DGL 790, DGL 700, and DGL 600, respectively, versus DGL 580 for the VerTech process.

Check the consistency of the data, and offer an opinion as to the problems that might occur if the process operated on a 20% sludge solution in water.

2. The term BLEVE (boiling-liquid expanding-vapor explosion) refers to an explosion that occurs when the pressure on a liquid is suddenly reduced substantially below its vapor pressure. Explain how such an explosion can occur. Might it occur if a tank car ruptures in an accident even if no fire occurs? Give one or two other examples of vessel failures that might cause a BLEVE.

16.2 Modeling and Predicting Vapor Pressure as a Function of Temperature

How can you find the answer if you don't know the question?

M.C. Sonby, Shell Development Co.

In this section we are going to explain how to determine values for the vapor pressure given the temperature, or the temperature given the vapor pressure. Several aids exist for you to use: (a) Equations of p^* as a function of T ; (b) charts of p^* versus T ; (c) tables of p^* versus T ;

Dr. Sonby reported at one of the A.I.ChE. meetings that

"In one of my first projects at Shell, I was trying to determine the rate of emission of sulfur vapor from a pit full of molten sulfur. I was able to locate four different references on the vapor pressure of molten sulfur. Unfortunately, all four references gave different vapor pressures, with the highest and lowest being an order of magnitude apart! As it turned out, the experimental methods used to determine the vapor pressures varied greatly, as did the purity of the sulfur in the experiments."

Thus, you need to be able to appraise the accuracy of the predictions of values of the vapor pressure of even old standbys.

16.2-1 Prediction via Equations

You can see from Figure 16.2 that the function of p^* versus T is not a linear function (except as an approximation over a very small temperature range). Many functional forms have been proposed to predict p^* from T (refer to Ruzicka, K., and

V. Majer, "Simple and Controlled Extrapolation of Vapor Pressures toward the Triple Point," *A.I.ChE.J.*, **42**, 1723–1740 [1996] for an evaluation of numerous equations) and the reverse, some with numerous coefficients. We will use the **Antoine equation** in this book—it has sufficient accuracy for our needs, and coefficients for the equation for over 5,000 compounds exist in the literature:

$$\ln p^* = A - \frac{B}{C + T} \quad (16.2)$$

where A , B , C = constants for each substance

T = temperature, K

Refer to Appendix G for the values of A , B , and C for a small set of compounds. The CD in the back of this book, based on data provided by Yaws,* will enable you to retrieve vapor pressures for over 700 compounds. The National Institute of Standards and Technology has a program (www.nist.gov/srd/nist87.htm) that calculates the vapor pressures and displays tables for approximately 6,000 pure compounds.

You can estimate the values of A , B , and C in Equation (16.2) from experimental data by using a regression program such as the one in Polymath on the CD that accompanies this book. With just three experimental values for the vapor pressure versus temperature you can fit Equation (16.2).

EXAMPLE 16.1 Vaporization of Metals for Thin Film Deposition

Three methods of providing vaporized metals for thin film deposition are evaporation from a boat or from a filament and transfer via an electronic beam. Figure E16.1 illustrates evaporation from a boat placed in a vacuum chamber.

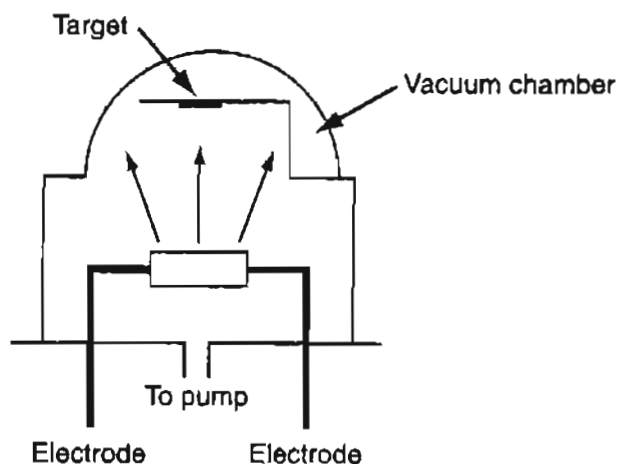


Figure E16.1

*Yaws, C. L., and H. C. Yang. "To Estimate Vapor Pressure Easily," *Hydrocarbon Processing*, p. 65 (October 1989).

The boat made of tungsten has a negligible vapor pressure at 972°C, the operating temperature for the vaporization of aluminum (which melts at 660°C and fills the boat). The approximate rate of evaporation m is given in g/(cm²)(s) by

$$m = 0.437 \frac{p^*(MW)^{1/2}}{T^{1/2}}$$

where p^* is the vapor pressure in kPa and T is the temperature in K.

What is the vaporization rate for Al at 972°C in g/(cm²)(s)?

Solution

You have to calculate p^* for Al at 972°C. The Antoine equation is suitable if data are known for the vapor pressure of Al. Considerable variation exists in the data for Al at high temperatures, but for Equation (16.2) we will use $A = 8.779$, $B = 1.615 \times 10^4$, and $C = 0$ with p^* in mm Hg and T in K.

$$\ln p_{972^\circ\text{C}}^* = 8.799 - \frac{1.615 \times 10^4}{972 + 273} = -4.17288$$

$$p_{972^\circ\text{C}}^* = 0.0154 \text{ mm Hg (0.00205 kPa)}$$

$$m = 0.437 \frac{(0.00205)(26.98)^{1/2}}{(972 + 273)^{1/2}} = 1.3 \times 10^{-4} \text{ g/(cm}^2\text{)(s)}$$

16.2-2 Retrieving Vapor Pressures from the Tables

You can find the vapor pressures of substances listed in tables in handbooks, physical property books, and Internet sites. We will use water as an example. Tabulations of the properties of water and steam (water vapor) are commonly called the **steam tables**. Furthermore, when you retrieve the properties from a CD, such as the American Society of Mechanical Engineers' *Properties of Steam*, they probably were generated by an equation. We will often refer to the software on the CD in the back of this book that gives the properties of water and steam as the "steam tables." In this book you will also find a foldout in the back pocket that contains abbreviated steam tables in both AE and SI units. The CD in the back of this book will prove to be a time saver because you can obtain values for the properties of water in mixed units that are continuous over the permitted range of values, and avoid tedious single or double interpolation in tables.

Several types of tables exist in the foldout. The following examples are from the tables in SI and AE units:

1. A table for saturated water and vapor listing p^* versus T as well as other properties such as the specific volume of the liquid (\hat{V}_l) and vapor (\hat{V}_g).

Properties of Saturated Water in SI Units

Press. kPa	T K	Volume, m ³ /kg	
		V_l	V_g
0.80	276.92	0.001000	159.7
1.0	280.13	0.001000	129.2
1.2	282.81	0.001000	108.7
1.4	285.13	0.001001	93.92
1.6	287.17	0.001001	82.76
1.8	288.99	0.001001	74.03
2.0	290.65	0.001002	67.00
2.5	294.23	0.001002	54.25
3.0	297.23	0.001003	45.67
4.0	302.12	0.001004	34.80

2. A table of T for saturated water and vapor listing T versus p^* as well as other properties such as \hat{V} for the liquid and vapor.

Properties of Saturated Water in SI Units

T K	Press. kPa	Volume, m ³ /kg	
		\hat{V}_l	\hat{V}_g
273.16	0.6113	0.001000	206.1
275	0.6980	0.001000	181.7
280	0.9912	0.001000	130.3
285	1.388	0.001001	94.67
290	1.919	0.001001	69.67
295	2.620	0.001002	51.90
300	3.536	0.001004	39.10
305	4.718	0.001005	29.78
310	6.230	0.001007	22.91
315	8.143	0.001009	17.80

3. A table listing superheated vapor (steam) properties as a function of T and p , including the specific volume of the vapor v in lb/ft³.

Properties of Superheated Steam in AE Units

Abs. Press. lb/in. ² (Sat. Temp.)		Sat. Water	Sat. Steam	400°F	420°F	440°F
Sh				29.23	49.23	69.23
175	v	0.0182	2.601	2.730	2.814	2.897
(370.77)	h	343.61	1196.7	1215.6	1227.6	1239.9

Superheated Steam (continued)

Abs. Press. lb/in. ² (Sat. Temp.)		Sat. Water	Sat. Steam	400°F	420°F	440°F
180 (373.08)	<i>Sh</i>			26.92	46.92	66.92
	<i>v</i>	0.0183	2.532	2.648	2.731	2.812
	<i>h</i>	346.07	1197.2	1214.6	1226.8	1239.2
185 (375.34)	<i>Sh</i>			24.66	44.66	64.66
	<i>v</i>	0.0183	2.466	2.570	2.651	2.731
	<i>h</i>	348.47	1197.6	1213.7	1226.0	1238.4

4. A table of subcooled (liquid) water properties as a function of p and T ; ρ is the density; u and h are discussed in Chapter 21.

Properties of Liquid Water in SI Units

		<i>T</i> (K)		
		400	425	450
Sat.	$p_{\text{sat}}, \text{kPa} \times 10^{-3}$	0.2456	0.4999	0.9315
	$\rho, \text{kg/m}^3$	937.35	915.08	890.25
	$h, \text{kJ/kg}$	532.69	639.71	748.98
	$u, \text{kJ/kg}$	532.43	639.17	747.93
500	$\rho, \text{kg/m}^3$	937.51	915.08	
	$h, \text{kJ/kg}$	532.82	639.71	
	$u, \text{kJ/kg}$	532.29	639.17	
700	$\rho, \text{kg/m}^3$	937.62	915.22	
	$h, \text{kJ/kg}$	532.94	639.84	
	$u, \text{kJ/kg}$	532.19	639.07	

Take the foldout from the pocket in the back of this book, locate each table, and use it to follow the explanations below.

How can you tell which table to use to get the properties you want? One way is to locate the state of interest on a phase diagram for water. The other is to plow through the steam tables.

For example, do the conditions of 25°C and 4 atm refer to liquid water, a saturated liquid–vapor mixture, or water vapor? Examine Figure 16.7. The state occurs to the left of the saturated liquid curve in the tiny space between the saturated liquid line and the vertical axis on the 298K isotherm (just below the 300K isotherm). Note that the 25°C (298K) isotherm in the liquid region goes so straight up the chart that it is essentially a vertical line extending from the intersection of 298K and the saturated liquid curve. You can use the values in the steam tables plus what you know about phase to reach a decision about the state of the water. In the SI steam tables of T versus p^* for

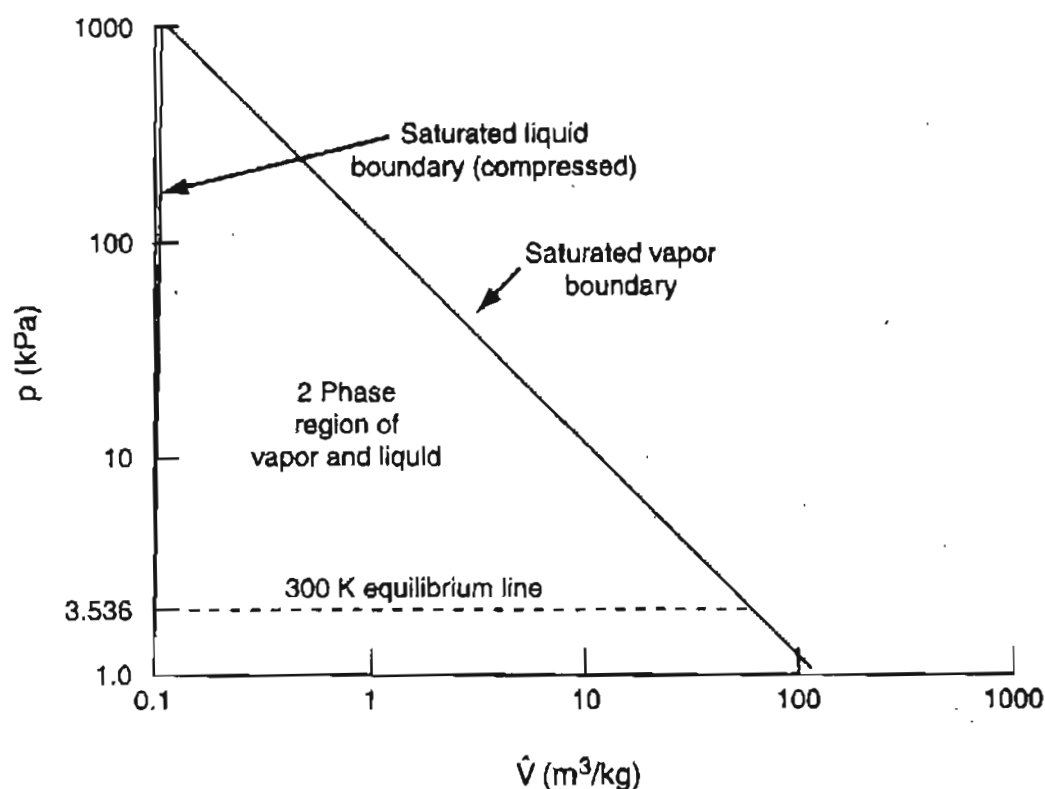


Figure 16.7 Portion of the p - \hat{V} phase diagram for water. (Note that the axes are logarithmic scales).

saturated water, T is just less than 300K at which $p^* = 3.536$ kPa, hence p^* will be a bit less than 3.536 kPa. Because the given pressure is about 400 kPa, much higher than the saturation pressure at 298K, clearly the water is subcooled (compressed liquid).

Can you locate the point $p^* = 250$ kPa and $\hat{V} = 1.00$ m³/kg? Do you find the water is in the superheated region? The specified volume is larger than the saturated vapor volume of 0.7187 m³/kg at 250 kPa. What is the state corresponding to $T = 300$ K and $\hat{V} = 0.505$ m³/kg? Water at that state is a mixture of saturated liquid and vapor. You can calculate the quality of the water–water vapor mixture using Equation (16.1) as follows. From the steam tables the specific volumes of the saturated liquid and vapor are

$$\hat{V}_\ell = 0.001004 \text{ m}^3/\text{kg} \quad \hat{V}_g = 39.10 \text{ m}^3/\text{kg}$$

Basis: 1 kg of wet steam mixture

Let x = mass fraction vapor. Then

$$\frac{0.001004 \text{ m}^3}{1 \text{ kg liquid}} \left| \frac{(1 - x) \text{ kg liquid}}{1 \text{ kg liquid}} \right| + \frac{39.10 \text{ m}^3}{1 \text{ kg vapor}} \left| \frac{x \text{ kg vapor}}{1 \text{ kg vapor}} \right| = 0.505 \text{ m}^3$$

$$x = 0.0129 \text{ (the fractional quality)}$$

If you are given a specific mass of saturated water plus steam at a specified temperature or pressure so that you know the state of the water is in the two-phase region, you can use the steam tables for various calculations. For example, suppose a 10.0 m^3 vessel contains 2000 kg of water plus steam at 10 atm , and you are asked to calculate the volume of each phase. Let the volume of water be V_ℓ and the volume of steam be V_g ; then the masses of each phase are V_ℓ/\hat{V}_ℓ and V_g/\hat{V}_g , respectively. From your knowledge of the total volume and total mass:

$$V_\ell + V_g = 10$$

and

$$V_\ell/\hat{V}_\ell + V_g/\hat{V}_g = 2000$$

You can find from the steam tables that the specific volumes are $\hat{V}_\ell = 0.0011274 \text{ m}^3/\text{kg}$ and $\hat{V}_g = 0.19430 \text{ m}^3/\text{kg}$. Solving these simultaneous equations for V_ℓ and V_g gives the volume of the liquid as 2.21 m^3 , and the volume of the steam as 7.79 m^3 . The mass of the liquid is 1960 kg , and the mass of the steam is 40 kg .

Because the values in the steam tables are tabulated in discrete increments, for intermediate values you will have to interpolate to retrieve values between the discrete values. (If interpolation does not appeal to you, use the steam tables on the CD in the back of this book.) The next example shows how to carry out interpolations in tables.

EXAMPLE 16.2 Interpolating in the Steam Tables

- (a) What is the saturation pressure of water at 312K ?
- (b) Steam is cooled from 640°F and 92 psia to 480°F and 52 psia . What is $\Delta\hat{V}$ in ft^3/lb ?

Solution

- (a) To solve this problem you have to carry out a single interpolation. Look in the steam tables under the properties of saturated water to get p^* so as to bracket 312K :

$T(\text{K})$	$p^* (\text{kPa})$
310	6.230
315	8.143

Figure E16.2 shows the concept of a linear interpolation between 310K and 315K . Find the change of p^* per unit change in T .

$$\frac{\Delta p^*}{\Delta T} = \frac{(8.143 - 6.230) \text{ kPa}}{(315 - 310) \text{ K}} = \frac{1.91}{5} = 0.383$$

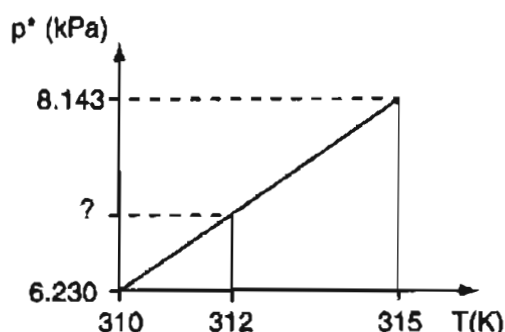


Figure E16.2

Multiply the fractional change and the number of degrees increase from 310K to get the change in p^* , and add the result to the value of p^* at 310K of 6.230 kPa:

$$\begin{aligned}
 p^*_{312\text{K}} &= p^*_{310\text{K}} + \frac{\Delta p^*}{\Delta T} (T_{312} - T_{310}) \\
 &= 6.230 + 0.383 (2) = 7.00 \text{ kPa}
 \end{aligned}$$

- (b) This problem requires double interpolation in the steam tables.

Set up the double interpolation as shown below. The volumes in the table below are in ft^3/lb . The first step is to get data for \hat{V} that bracket both 92 psia and 640°F as listed in columns 1, 3, and 4. The second step is to interpolate to get \hat{V} at the intermediate pressure of 92 psia (see column 2) for 600°F (6.768) and then 700°F (7.437) as listed in the fifth and sixth columns, respectively.

p (psia)	$T(^{\circ}\text{F})$		$T(^{\circ}\text{F})$		
	600	700	600	700	640
90	6.916	7.599	6.768	7.437	7.036
92	6.547	7.195			
95					
p (psia)	$T(^{\circ}\text{F})$		$T(^{\circ}\text{F})$		
	450	500	450	500	480
50	10.69	11.30	10.295	10.88	10.646
52	9.703	10.26			
55					

The final step is to interpolate at $p = 92$ psia between 600°F and 700°F to get $\hat{V} = 7.036 \text{ ft}^3/\text{lb}$ at 640° and 92 psia. Repeat the procedure for 52 psia to get $\hat{V} = 10.646 \text{ ft}^3/\text{lb}$ at 480°F. Finally, calculate

$$\Delta \hat{V} = 10.646 - 7.036 = 3.61 \text{ ft}^3/\text{lb}$$

Could you have interpolated first in temperature and then in pressure? Of course.

16.2-3 Predicting Vapor Pressures from Reference Substance Plots

Because of the curvature of the vapor pressure versus temperature data (see Figure 16.2), no simple equation with two or three coefficients will fit the data accurately from the triple point to the critical point. Othmer proposed in numerous articles (see, for example, Othmer, D.F., *Ind. Eng. Chem.* **32**, 841(1940) and Perry, J.H., and E.R. Smith, *Ind. Eng. Chem.*, **25**, 195 (1933)) that **reference substance plots** (the name will become clear in a moment) could convert the vapor pressure versus temperature curve into a straight line. One well-known example is the Cox chart (Cox, E.R., *Ind. Eng. Chem.*, **15**, 592[1923]). You can use the Cox chart to retrieve vapor pressure values to test the reliability of experimental data, to interpolate, and to extrapolate. Figure 16.8 is a Cox chart. Here is how you can make a Cox chart.

1. Mark on the horizontal scale values of $\log p^*$ so as to cover the desired range of p^* for the compound of interest.
2. Next draw a straight line on the plot at a suitable angle, say 45° , that covers the range of T that is to be marked on the vertical axis.

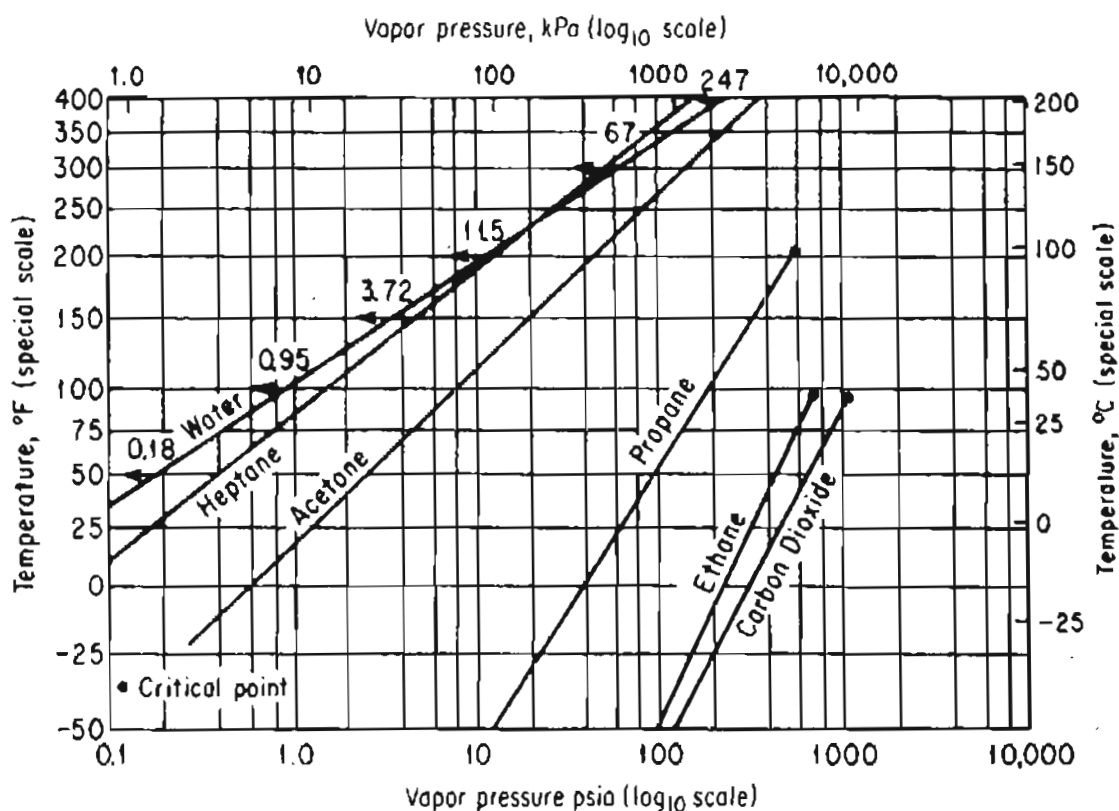


Figure 16.8 Cox chart. The vapor pressure of compounds other than water is observed to fall on straight lines when plotted on the special scales developed for the Cox chart by using a reference substance (here water).

3. To calibrate the vertical axis in common integers such as 25, 50, 100, 200 degrees, and so on, you use a **reference substance**, namely water. For the index mark for the first integer, say 100°F, you look up the vapor pressure of water at 100°F in the steam tables, or calculate it from the Antoine equation, to get 0.9487 psia. Locate 0.9487 psia on the horizontal axis, and proceed vertically until you hit the 45° straight line. Then proceed horizontally left until you hit the vertical axis. Mark the scale at the intersection as 100°F.
4. Pick the next temperature, say 200°F, for which the vapor pressure of water is 11.525 psia. From 11.525 psia on the horizontal axis proceed vertically to the 45° straight line, and then horizontally to the vertical axis. Mark the scale at the intersection with the vertical axis as 200°F.
5. Continue as in 3 and 4 until the vertical scale is established over the desired range for the temperature.

A plot of the temperature versus vapor pressure for other compounds will yield straight lines, as shown in Figure 16.8. What proves useful about the Cox chart is that the vapor pressures of other substances plotted on this specially prepared set of coordinates will yield straight lines over extensive temperature ranges, and thus facilitate the extrapolation and interpolation of vapor-pressure data. It has been found that lines so constructed for closely related compounds, such as hydrocarbons, all meet at a common point. Since straight lines can be obtained in a Cox chart, only *two points* of vapor-pressure data are needed to provide complete information about the vapor pressure of a substance over a considerable temperature range.

Lets look at an example of preparing and using a Cox chart.

EXAMPLE 16.3 Extrapolation of Vapor-Pressure Data

The control of solvents was first described in the *Federal Register*, v. 36, no. 158, August 14, 1971, under Title 42, Chapter 4, Appendix 4.0, Control of Organic Compound Emissions. Chlorinated solvents and many other solvents used in industrial finishing and processing, dry-cleaning plants, metal degreasing, printing operations, and so forth, can be recycled and reused by the introduction of carbon adsorption equipment. To predict the size of the adsorber, you first need to know the vapor pressure of the compound being adsorbed at the process conditions.

The vapor pressure of chlorobenzene is 400 mm Hg at 110°C and 5 atm at 205°C. Estimate the vapor pressure at 245°C and also at the critical point (359°C).

Solution

The vapor pressures will be estimated by use of a Cox chart. You construct the temperature scale (vertical) and vapor pressure scale (horizontal), as described in connection with Figure 16.8. Prepare the horizontal axis on the chart by marking

a log (or ln) scale from 0.1 to 10^4 . Mark the vapor pressures of water from 3.72 to 3094 psia corresponding to 150°F to 700°F, and mark the respective integer temperatures marked on the vertical scale, as shown in Figure E16.3.

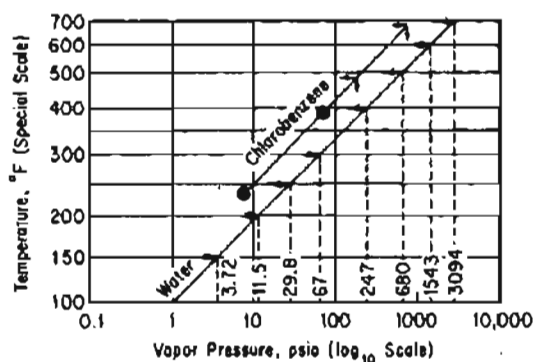


Figure E16.3

Next convert the two given vapor pressures of chlorobenzene into psia

$$\frac{400 \text{ mm Hg}}{760 \text{ mm Hg}} \left| \frac{14.7 \text{ psia}}{1 \text{ atm Hg}} \right| = 7.74 \text{ psia} \quad 110^\circ\text{C} = 230^\circ\text{F}$$

$$\frac{5 \text{ atm Hg}}{1 \text{ atm Hg}} \left| \frac{14.7 \text{ psia}}{1 \text{ atm Hg}} \right| = 73.5 \text{ psia} \quad 205^\circ\text{C} = 401^\circ\text{F}$$

and plot these two points on the graph paper. Examine the encircled dots. Finally, draw a straight line between the encircled points and extrapolate to 471°F (245°C) and 678°F (359°C). At these two temperatures, you can read off the estimated vapor pressures.

	<u>471°F (245°C)</u>	<u>678°F (359°C)</u>
Estimated:	150 psia	700 psia
Experimental:	147 psia	666 psia

Experimental values are given for comparison.

You could have made a Cox chart using SI units if you wanted to save the conversions.

EXAMPLE 16.4 Solvent Selection Based on OSHA PEL Limits and Potential Hazard

The limitations because of toxicity of chemicals established by the Occupational Safety and Health Administration (OSHA) as permissible exposure limits (PEL) can be used to estimate the relative hazard of solvents. Also, the relative

vapor pressures of solvents can be used as a measure of occupational exposure. Based on the following data for the OSHA PEL

	<u>OSHA PEL (in air), ppm by volume</u>
Ethyl acetate	400
Methyl ethyl ketone	200
n-butyl acetate	1.3

estimate the relative hazards of the three solvents taking into account both toxicity and exposure.

Solution

A combined hazard criterion would be to take the inverse of the OSH PEL as a potential hazard due to toxicity and multiply by the pertinent vapor pressure, a measure of exposure. The vapor pressures of the respective compounds at 25°C are:

	<u>p* (mm Hg)</u>
Ethyl acetate	96.9*
Methyl ethyl ketone	94.8*
n-butyl acetate	20**

*From the CD

**From Perry

The combined criteria in increasing order of hazard are:

Ethyl acetate:	$96.9/400 = 0.24$
Methyl ethyl ketone	$94.8/200 = 0.47$
n-butyl acetate	$20/1.3 = 15.4$

Clearly n-butyl acetate would be the poorest choice from the viewpoint of its hazardous nature.

Although this chapter treats the vapor pressure of a pure component, we should mention that the term vapor pressure has been applied to solutions of multiple components as well. For example, to meet emission standards, refiners formulate gasoline and diesel fuel differently in the summer than in the winter. The rules on emissions are related to the vapor pressure of a fuel, which is specified in terms of the *Reid Vapor Pressure (RVP)*, a value that is determined at 100°F in a bomb that permits partial vaporization. For a pure component the RVP is the true vapor pressure, but for a mixture (as are most fuels) the RVP is lower than the true vapor pressure of the mixture (by roughly 10% for gasoline). Refer to Vazquez-Esparragoza, J. J., G. A. Iglesias-Silva, M. W. Hlavinka, and J. Bulin. "How to Estimate RVP of Blends," *Hydrocarbon Processing*, 135 (August 1992), for specific details about estimating the RVP.

SELF-ASSESSMENT TEST

Questions

1. Metallic lead can be recovered by smelting of the battery plates in lead-acid batteries. If the plates are composed of 50% lead sulfate and 50% metallic lead, how would you suggest eliminating most lead emissions from the process?
2. A solid can vaporize into a gas without going through a liquid phase. What form of an equation would you recommend to represent the pressure of the gas when it is at equilibrium with the solid?
3. Do the steam tables, and similar tables for other compounds, provide more accurate values of the vapor pressure than use of the Antoine equation, or modifications of it?
4. Is it possible to prepare a Cox chart for water?

Problems

1. Describe the state and values of the pressure of water initially at 20°F as the temperature is increased to 250°F in a fixed volume.
2. Look in Appendix J at the diagram for CO₂.
 - a. At what pressure is CO₂ solid in equilibrium with both CO₂ liquid and vapor?
 - b. What happens if the solid is placed in the atmosphere?
3. Use the Antoine equation to calculate the vapor pressure of ethanol at 50°C, and compare the result with the experimental value.
4. Determine the normal boiling point of benzene from the Antoine equation.
5. Prepare a Cox chart from which the vapor pressure of toluene can be predicted over the temperature range -20 to 140°C.
6. Make a large copy of Figure SAT16.2P6, a substance that contracts on freezing like most

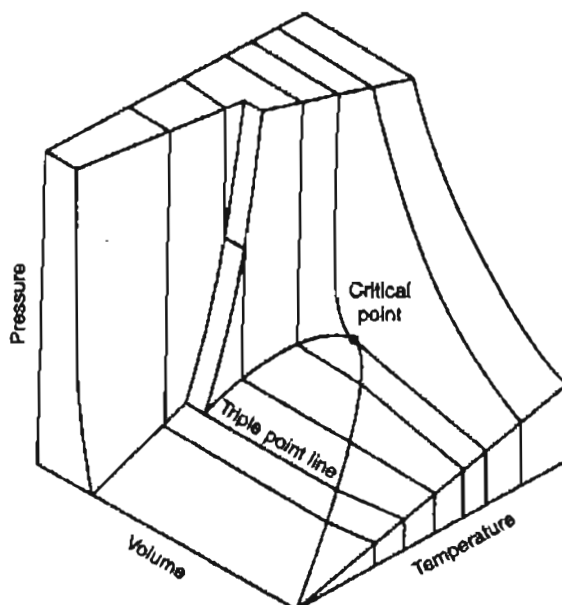


Figure SAT16.2P6

substances (except water), and on the copy label all of the boundaries that represent equilibria between the phases. Also label the surface to show where the solid, liquid, and vapor regions themselves occur.

7. In Figure SAT16.2P7 label the axes and the contours on the special phase chart for water with the appropriate symbols for the variables involved.

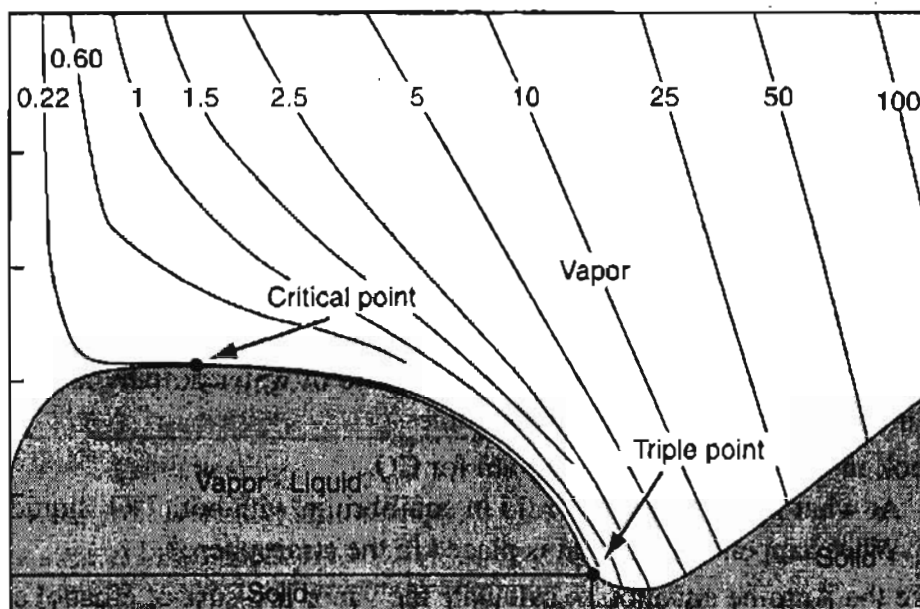


Figure SAT16.2P7

Thought Problems

1. In the start-up of a process, Dowtherm, an organic liquid with a very low vapor pressure, was being heated from room temperature to 335°F. The operator suddenly noticed that the gauge pressure was not the expected 15 psig but instead was 125 psig. Fortunately, a relief valve in the exit line ruptured into a vent (expansion) tank so that a serious accident was avoided.

Why was the pressure in the exit line so high?

2. A cylinder containing butadiene exploded in a research laboratory, killing one employee. The cylinder had been used to supply butadiene to a pilot plant. When butadiene gas was required, heat was supplied to the cylinder to raise the pressure of the butadiene in the tank. The maximum temperature that could be achieved in the tank on subsequent tests with a like tank was 160°C. At 152°C, the critical temperature for butadiene, the pressure in 628 lb_f/in.², less than one-half of the pressure required to rupture the tank by hydraulic test.

Why did the tank explode?

3. "Careless Campers Contaminate Mountain Water" was a recent headline in the newspaper. The article went on:

Beware! There are little monsters loose in those seemingly clean, pristine mountain streams. Their name: *Giardia*, and of specific interest to humans and pigs, *Giardia lamblia*. *Giardia* is a beet-shaped organism with no less than eight flagella. It is of concern to anyone who happens to slurp any down because it attaches itself by means of a sucking organism to the intestinal mucous membranes. The result is severe diarrhea, bordering on dysentery.

The incidence of *Giardia* in the wilderness areas of New Mexico and Colorado has vastly increased over the past five years. The disease it causes, giardiasis, is contracted by drinking water containing the organism. Unfortunately for all backpackers, horse packers, and day hikers, many of the lakes and streams are already tainted. No problem, you say—just drop in a chemical purification tablet and let it do the job? While chemical purification such as Halazone, iodine, or chlorine may kill many bacteria, the hale and hearty *giardia* goes unscathed.

What steps would you take to avoid the problem other than carrying a potable water supply with you? You need at least 210°F to kill the organisms by boiling water.

Discussion Problems

1. The following has been taken from the Science Essays of Dr. Ronald DeLorenzo with permission.

WHY HOT-WATER PIPES FREEZE BEFORE COLD WATER PIPES

Houses without cellars or basements usually have a crawl space between the ground and the first floor for servicing plumbing. People living in houses with crawl spaces may find their water pipes frozen after a very cold winter night. To their surprise, it is usually the hot-water pipe that is frozen and not the cold-water pipe. Hot water pipes freeze before cold water pipes. Let's see if we can explain why this occurs. Can you dissolve more gas in hot water or in cold water?

More gas can be dissolved in cold water than in hot water. Most students answering this question for the first time give the wrong answers, probably because they know that hot water will dissolve more solid solutes (like salt and sugar) than cold water. However, colder solvents dissolve more gas than warmer solvents. One reason soda pop is refrigerated is to keep it from losing its carbonation and going flat. Warm soda pop goes flat faster than cold soda pop.

You've probably observed a related phenomenon when heating water to the boiling point. Before boiling occurs, many little gas bubbles you see are dissolved air coming out of solution.

When water is heated in a hot-water heater, the water is degassed. Dissolved air escapes from cold water as it is heated in a hot-water heater. Water in a hot-water pipe (supplied by the hot-water heater) contains less dissolved gas than water in a cold-water pipe.

Now can you explain why the hot-water pipe freezes before the cold-water pipe freezes? (For the answer refer to www.educationcenter.org/lorenzo.html.)

2. Many distillation columns are designed to withstand a pressure of 25 or 50 psig. The reboiler at the bottom of the column is where the heat used to vaporize the fluid in the column is introduced. What would you recommend as to the type of heat source among these three: (1) steam (heat exchanger), (2) fired heater (analogous to a boiler), and (3) hot oil (heat exchanger)?

GLOSSARY OF NEW WORDS

Antoine equation Equation that relates vapor pressure to absolute temperature.

Boiling Change from liquid to vapor.

Bubble point The temperature at which liquid changes to vapor (at some pressure).

Condensation The change of phase from vapor to liquid.

Degrees of superheat The difference in temperature between the actual T and the saturated T at a given pressure.

Dew point The temperature at which the vapor just begins to condense at a specified pressure, that is, the values of the temperature along the vapor pressure curve.

Equilibrium A state of the system in which there is no tendency to spontaneously change.

Evaporation The change of phase of a substance from liquid to vapor.

Freezing The change of phase of a substance from liquid to solid.

Fusion See Melting.

Melting The change of phase of a substance from solid to liquid.

Noncondensable gas A gas at conditions under which it cannot condense to a liquid or a solid.

Normal boiling point The temperature at which the vapor pressure of a substance (p^*) is 1 atm (101.3 kPa).

Normal melting point The temperature at which a solid melts at 1 atm (101.3 kPa).

Phase diagram Representation of the different phases of a compound on a two- (or three-) dimensional graph.

Quality Fraction or percent of a liquid-vapor mixture that is vapor (wet vapor).

Reference substance The substance used as the reference in a reference substance plot.

Reference substance plot A plot of a property of one substance versus the same property of another (reference) substance that results in an approximate straight line.

Saturated liquid Liquid that is in equilibrium with its vapor.

Saturated vapor Vapor that is in equilibrium with its liquid.

Sublimation Change of phase of a solid directly to a vapor.

Sublimation pressure The pressure given by the melting curve (a function of temperature).

Superheated vapor Vapor at values of temperatures and pressure exceeding those that exist at saturation.

Steam tables Tabulations of the properties of water and steam (water vapor).

Subcooled liquid Liquid at values of temperature and pressure less than those that exist at saturation.

Supercritical region A portion of a physical properties plot in which the substance is at combined p - T values above the critical point.

Triple point The one p - T - V combination at which solid, liquid, and vapor are all in equilibrium.

Two-phase (region) Region on a plot of physical properties in which two phases exist simultaneously.

Vapor A gas below its critical point in a system in which the vapor can condense.

Vaporization The change from liquid to vapor of a substance.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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Web Sites

<http://antoine.fsu.umd.edu⪙liquids/faq/antoine-vapor-pressure.shtml>

<http://chemengineer.about.com/library/weekly/aa082800a.htm>

<http://www.questconsult.com/~jrm/dewbub.html>

<http://www.taftan.com/steam.htm>

PROBLEMS

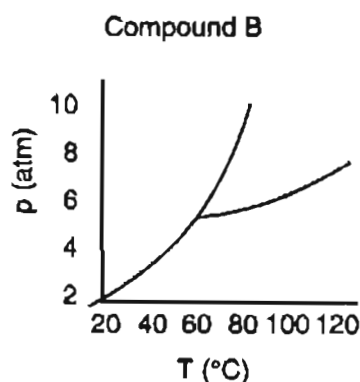
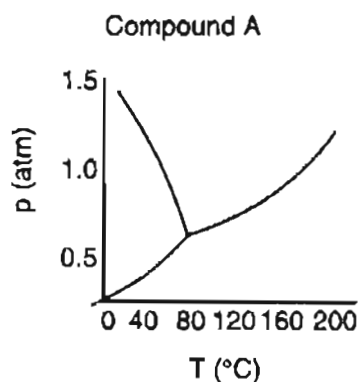
***16.1** Select the correct answer(s) in the following statements:

1. In a container of 1.00 L of toluene, the vapor pressure of the toluene is 103 mm Hg. The same vapor pressure will be observed in a container of (1) 2.00 L of toluene at the same temperature; (2) 1.00 L of toluene at one-half the absolute temperature; (3) 1.00 L of alcohol at the same temperature; (4) 2.00 L of alcohol at the same temperature.
2. The temperature at which a compound melts is the same temperature at which it (1) sublimes; (2) freezes; (3) condenses; (4) evaporates.
3. At what pressure would a liquid boil first? (1) 1 atm; (2) 2 atm; (3) 200 mm Hg; (4) 101.3 kPa.
4. When the vapor pressure of a liquid reaches the pressure of the atmosphere surrounding it, it will (1) freeze; (2) condense; (3) melt; (4) boil.
5. Sublimation is the phase change from (1) the solid phase to the liquid phase; (2) the liquid phase to the solid phase; (3) the solid phase to the gas phase; (4) the gas phase to the solid phase.
6. A liquid that evaporates rapidly at ambient conditions is more like than not to have a (1) high vapor pressure; (2) a low vapor pressure; (3) a high boiling point; (4) strong attraction among the molecules.

***16.2** Based on the following phase diagrams, answer the questions below, and explain your answers.

(a) What is the approximate normal melting point for compound A?

(b) What is the approximate normal boiling point for compound A?



(c) What is the approximate triple point temperature for compound B?

(d) Which compounds sublime at atmospheric pressure?

- *16.3 Figure P16.3 is a phase diagram for a pure compound. On a copy of the diagram place the name in the following list next to the associated letter in the diagram:

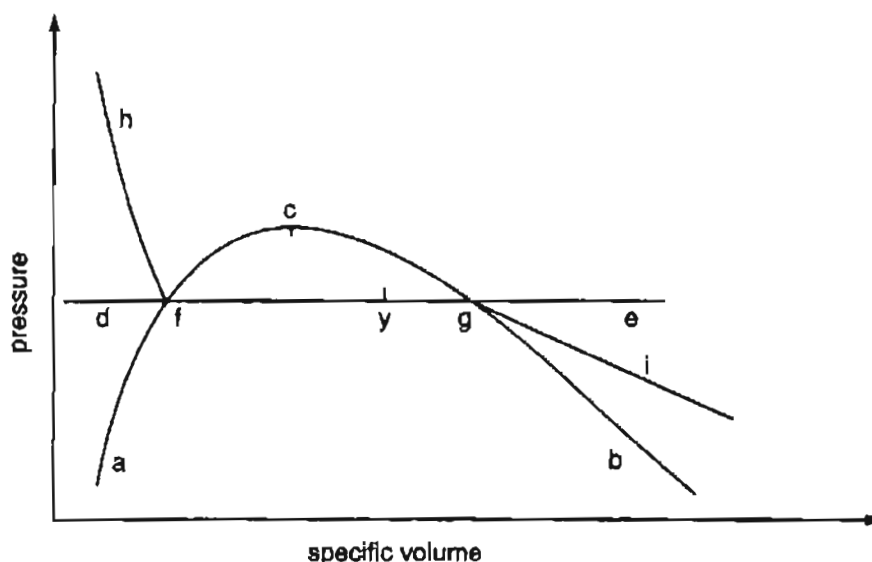


Figure P16.3

- (a) the saturated curve
- (b) the saturated liquid curve
- (c) the saturated vapor curve
- (d) the liquid phase
- (e) the vapor phase
- (f) the liquid–vapor two phase region
- (g) the critical point
- (h) a constant temperature line
- (i) a constant pressure line

- *16.4 Draw a p - T diagram for a pure component. Label the curves and points that are listed in P16.3 on it.

- *16.5 One form of cooking is to place the food in a pressure cooker (a sealed pot). Pressure cookers decrease the time require to cook the food.

Some explanations of how a pressure cooker works are as follows. Which of the explanations are correct?

- (a) We know $p_1 T_1 = p_2 T_2$. So if the pressure is doubled, the temperature should be doubled and resulting to quicker cooking.
- (b) Pressure cookers are based on the principle that $p \propto T$, i.e., pressure is directly proportional to temperature. With the volume kept constant, if you increase the pressure, the temperature also increases, and it takes less time to cook.
- (c) Food cooks faster because the pressure is high. This means that there are more impacts of molecules per surface area, which in turn increases the temperature of the food.

- (d) If we increase the pressure under which food is cooked, we have more collisions of hot vapor with the food, cooking it faster. On an open stove, vapor escapes into the surroundings, without affecting the food more than once.
- (e) As the pressure inside the sealed cooker builds, as a result of the vaporization of water, the boiling point of water is increased, thereby increasing the temperature at which the food cooks—hotter temperature, less time.

***16.6** Answer the following questions true or false:

- (a) The vapor pressure curve separates the liquid phase from the vapor phase in a p - T diagram.
- (b) The vapor pressure curve separates the liquid phase from the vapor phase in a p - V diagram.
- (c) The freezing curve separates the liquid phase from the solid phase in a p - T diagram.
- (d) The freezing curve separates the liquid phase from the solid phase in a p - V diagram.
- (e) At equilibrium at the triple point, liquid and solid coexist.
- (f) At equilibrium at the triple point, solid and vapor coexist.

***16.7** Explain how the pressure for a pure component changes (higher, lower, no change) for the following scenarios:

- (a) A system containing saturated liquid is compressed at constant temperature.
- (b) A system containing saturated liquid is expanded at constant temperature.
- (c) A system containing saturated liquid is heated at constant volume.
- (d) A system containing saturated liquid is cooled at constant volume.
- (e) A system containing saturated vapor is compressed at constant temperature.
- (f) A system containing saturated vapor is expanded at constant temperature.
- (g) A system containing saturated vapor is heated at constant volume.
- (h) A system containing saturated vapor is cooled at constant volume.
- (i) A system containing vapor and liquid in equilibrium is heated at constant volume.
- (j) A system containing vapor and liquid in equilibrium is cooled at constant volume.
- (k) A system containing a superheated gas is expanded at constant temperature.
- (l) A system containing superheated gas is compressed at constant temperature.

***16.8** Ice skates function because a lubricating film of liquid forms immediately below the small contact area of the skate blade. Explain by means of diagrams and words why this liquid film appears on ice at 25°F.

****16.9** Methanol has been proposed as an alternate fuel for automobile engines. Proponents point out that methanol can be made from many feedstocks such as natural gas, coal, biomass, and garbage, and that it emits 45% less ozone precursor gases than does gasoline. Critics say that methanol combustion emits toxic formaldehyde and that methanol rapidly corrodes automotive parts. Moreover, engines using methanol are hard to start at temperatures below 40°F. Why are engines hard to start? What would you recommend to ameliorate the situation?

***16.10** Calculate the vapor pressure of each compound listed below at the designated temperature using the Antoine equation and the coefficients in Appendix G. Compare your results with the corresponding values of the vapor pressures obtained from the Antoine equation found in the physical properties package on the CD accompanying this book.

(a) Acetone at 0°C

(b) Benzene at 80°F

(c) Carbon tetrachloride at 300 K

✓ ****16.11** Estimate the vapor pressure of ethyl ether at 40°C using the Antoine equation based on the experimental values as follows:

p^* (kPa):	2.53	15.0	58.9
T (°C):	-40.0	-10.0	20.0

***16.12** At the triple point, the vapor pressures of liquid and solid ammonia are respectively given by $\ln p^* = 15.16 - 3063/T$ and $\ln p^* = 18.70 - 3754/T$ where p is in atmospheres and T is in kelvin. What is the temperature at the triple point?

***16.13** In a handbook the vapor pressure of solid decaborane ($B_{10}H_{14}$) is given as

$$\log_{10} p^* = 8.3647 - \frac{2642}{T}$$

and of liquid $B_{10}H_{14}$

$$\log_{10} p^* = 10.3822 - \frac{3392}{T}$$

The handbook also shows the melting point of $B_{10}H_{14}$ is 89.8°C. Can this be correct?

***16.14** Calculate the normal boiling point of benzene and of toluene using the Antoine equation. Compare your results with listed data in a handbook or data base.

****16.15** Numerous methods are employed to evaporate metals in thin film deposition.

The rate of evaporation is

$$W = 5.83 \times 10^{-2} \frac{p_v M^{1/2}}{T^{1/2}} \text{ g/(cm}^2\text{)(s)} \quad (p_v \text{ in torr, } T \text{ in K, } M = \text{molecular weight})$$

Since p_v is also temperature-dependent, it is necessary to define further the vapor pressure-temperature relationship for this rate equation. The vapor pressure model is

$$\log_{10} p_v = A - \frac{B}{T}$$

where T is in K.

Calculate the temperature needed for an aluminium evaporation rate of $10^{-4} \text{ g/(cm}^2\text{)(s)}$. Data: $A = 8.79$, $B = 1.594 \times 10^4$.

- *16.16** Take 10 data points from the steam tables for the vapor pressure of water as a function of temperature from the freezing point to 500 K, and fit the following function:

$$p^* = \exp [a + b \ln T + c (\ln T)^2 + d (\ln T)^3]$$

where p is in kPa and T is in K.

- ✓ ***16.17** For each of the conditions of temperature and pressure listed below for water, state whether the water is a solid phase, liquid phase, superheated, or is a saturated mixture, and if the latter, indicate how you would calculate the quality. Use the steam tables (inside the back cover) to assist in the calculations.

State	p (kPa)	T (K)	\hat{V} (m ³ /kg)
1	2000	475	—
2	1000	500	0.2206
3	101.3	200	—
4	245.6	400	0.7308
5	1000	453.06	0.001127
6	200	393.38	0.8857

- *16.18** Repeat Problem 16.17 for the following conditions:

State	p (psia)	T (°F)	\hat{V} (ft ³ /lb)
1	0.3388	68	927.0
2	1661.6	610	0.0241
3	308.82	420	0.4012
4	180.0	440	2.812

- *16.19** Calculate the specific volume for water that exists at the following conditions:

- (a) $T = 100^\circ\text{C}$, $p = 101.4$ kPa, $x = 0.5$ (in m³/kg)
- (b) $T = 406.70$ K, $p = 300.0$ kPa, $x = 0.5$ (in m³/kg)
- (c) $T = 100.0^\circ\text{F}$, $p = 0.9487$ psia, $x = 0.3$ (in ft³/lb)
- (d) $T = 860.97^\circ\text{R}$, $p = 250$ psia, $x = 0.7$ (in ft³/lb)

- *16.20** Answer the following questions true or false:

- (a) A pot full of boiling water is tightly closed by a heavy lid. The water will stop boiling.
- (b) Steam quality is the same thing as steam purity.
- (c) Liquid water that is in equilibrium with its vapor is saturated.
- (d) Water can exist in more than three different phases.
- (e) Superheated steam at 300°C means steam at 300 degrees above the boiling point.
- (f) Water can be made to boil without heating it.

- *16.21 In a vessel with a volume of 3.00 m^3 you put 0.030 m^3 of liquid water and 2.97 m^3 of water vapor so that the pressure is 101.33 kPa . Then you heat the system until all of the liquid water just evaporates. What is the temperature and pressure in the vessel at that time?
- ✓ **16.22 In a vessel with a volume of 10.0 ft^3 you put a mixture of 2.01 lb of liquid water and water vapor. When equilibrium is reached the pressure in the vessel is measured as 80 psia . Calculate the quality of the water vapor in the vessel, and the respective masses and volume of liquid and vapor at 80 psia .
- **16.23 A vessel that has a volume of 0.35 m^3 contains 2 kg of a mixture of liquid water and water vapor at equilibrium with a pressure of 450 kPa . What is the quality of the water vapor?
- *16.24 A vessel with an unknown volume is filled with 10 kg of water at 90°C . Inspection of the vessel at equilibrium shows that 8 kg of the water is in the liquid state. What is the pressure in the vessel, and what is the volume of the vessel?
- *16.25 What is the velocity in ft/s when $25,000 \text{ lb/hr}$ of superheated steam at 800 psia and 900°F flows through a pipe of inner diameter 2.9 in. ?
- *16.26 Maintenance of a heater was carried out to remove water that had condensed in the bottom of the heater. By accident hot oil at 150°C was released into the heater when the maintenance man opened the wrong valve. The resulting explosion caused serious damage both to the maintenance man and to the equipment he was working on. Explain what happened during the incident when you write up the accident report.
- **16.27 Prepare a Cox chart for:
 (a) Acetone vapor
 (b) Heptane
 (c) Ammonia
 (d) Ethane
 from 0°C to the critical point (for each substance). Compare the estimated vapor pressure at the critical point with the critical pressure.
- **16.28 Estimate the vapor pressure of benzene at 125°C from the vapor pressure data

$T (^\circ\text{F})$:	102.6	212
$p^* (\text{psia})$:	3.36	25.5

by preparing a Cox chart.

- **16.29 Estimate the vapor pressure of aniline at 350°C based on the following vapor pressure data.

$T (^\circ\text{C})$	184.4	212.8	254.8	292.7
$p^* (\text{atm})$	1.00	2.00	5.00	10.00

- *16.30** Exposure in the industrial workplace to a chemical can come about by inhalation and skin adsorption. Because skin is a protective barrier for many chemicals, exposure by inhalation is of primary concern. The vapor pressure of a compound is one commonly used measure of exposure in the workplace. Compare the relative vapor pressures of three compounds added to gasoline: methanol, ethanol, and MTBE (methyl tertiary butyl ether), with their respective OSHA permissible exposure limits (PEL) that are specified in ppm (by volume):

Methanol	200
Ethanol	1000
MTBE	100

CHAPTER 17

TWO-PHASE GAS-LIQUID SYSTEMS (SATURATION, CONDENSATION, AND VAPORIZATION)

17.1 Saturation	510
17.2 Condensation	514
17.3 Vaporization	525

Your objectives in studying this chapter are to be able to:

1. Define what saturated gas means.
2. Explain how saturation of a vapor can occur in a noncondensable gas.
3. Calculate the partial pressure of the components of a saturated ideal gas given combinations of the temperature, pressure, volume, and/or number of moles present.
4. Calculate the number of moles of a vapor in a saturated gas given the pressure and the temperature.
5. Determine the condensation temperature (dew point) of the vapor in a saturated gas given the pressure, volume, and/or number of moles.

Why does it rain or snow? How can you predict the conditions of a mixture of a *pure vapor* (which can condense) and a *noncondensable gas* at equilibrium? Based on the discussion in Chapter 16 about phase diagrams and vapor pressure, you are now ready to consider the principles that will help you answer such questions.

Looking Ahead

In this chapter we explain what saturation means, why the concept is useful, and how to determine the composition and dew point of a saturated vapor in a noncondensable gas. We also discuss how condensation and vaporization relate to saturation.

17.1 Saturation

When any noncondensable gas (or a gaseous mixture) comes in contact with a liquid, the gas will acquire molecules from the liquid. If contact is maintained for a sufficient period of time, vaporization continues until equilibrium is attained, at which time the *partial pressure of the vapor in the gas will equal the vapor pressure of the liquid* at the temperature of the system. At equilibrium, the rate of vaporization is equal to the rate of condensation; therefore, the amount of liquid and the amount of vapor remain constant. As a result, regardless of the duration of contact between the liquid and gas, after equilibrium is reached no more net liquid will vaporize into the gas phase. The gas is then said to be **saturated** with the particular vapor at the given temperature. We also say that the gas mixture is at its dew point. **The dew point for the mixture of pure vapor and noncondensable gas means the temperature at which the vapor just starts to condense. At the dew point the partial pressure of the vapor is the vapor pressure.**

What is an example? You are familiar with air and water. At a given temperature, what is the partial pressure of the water in air when it is saturated? It is the vapor pressure (p^*) of water at that temperature. Suppose the partial pressure of the water vapor is less than p^* at some T . Can the gas be called saturated? No. Suppose the partial pressure of the water vapor is greater than p^* at T^* , the dewpoint. Will the gas be saturated? This is a nonsense question because at equilibrium the partial pressure of the water vapor cannot be greater than p^* at the dewpoint. Consider a gas partially saturated with water vapor at p and T . If the partial pressure of the water vapor is increased by increasing the total pressure on the system, eventually the partial pressure of the water vapor will equal p^* at T of the system. Because the partial pressure of water cannot exceed p^* at that temperature, a further attempt to increase the pressure on the system will result in water vapor condensing at constant T and p . Thus, p^* represents the maximum partial pressure that water can attain at a T^* .

Do you have to have both liquid and vapor present for saturation to occur? Really, no; only a minute drop of liquid at equilibrium with its vapor, or a minute amount of vapor in equilibrium with the liquid, will suffice.

What use can you make of the information or specification that a noncondensable gas is saturated? Once you know that a gas is saturated, you can determine the composition of the vapor–gas mixture from knowledge of the vapor pressure of the vapor (or equivalently the temperature of the saturated mixture) to use in material

balances. From Chapter 13 you should recall that under ambient conditions the ideal gas law applies to both air and water vapor with excellent precision. Thus, we can say that the following relations hold *at saturation*:

$$\frac{p_{\text{H}_2\text{O}}V}{p_{\text{air}}V} = \frac{n_{\text{H}_2\text{O}}RT}{n_{\text{air}}RT} \quad (17.1)$$

or

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{air}}} = \frac{p_{\text{H}_2\text{O}}^*}{p_{\text{air}}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}} = \frac{p_{\text{Total}} - p_{\text{air}}}{p_{\text{air}}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{Total}} - p_{\text{H}_2\text{O}}} \quad (17.2)$$

because V and T are the same for the air and water vapor.

Also

$$y_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{Total}}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{air}} + p_{\text{H}_2\text{O}}} = 1 - y_{\text{air}} \quad (17.3)$$

As a numerical example, suppose you have a saturated gas, say water in air at 51°C , and the pressure on the system is 750 mm Hg absolute. What is the partial pressure of the air? If the air is saturated, you know that the partial pressure of the water vapor is p^* at 51°C . You can look in a handbook, or use the steam tables, and find that $p^* = 98$ mm Hg. Then

$$p_{\text{air}} = 750 - 98 = 652 \text{ mm Hg}$$

Furthermore, the vapor air mixture has the following composition

$$y_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{Total}}} = \frac{98}{750} = 0.13$$

$$y_{\text{air}} = \frac{p_{\text{air}}}{p_{\text{Total}}} = \frac{652}{750} = 0.87$$

You can use these compositions when applying material balances.

EXAMPLE 17.1 Calculation of the Dew Point of the Products of Combustion

Oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ is burned at atmospheric pressure with 248% excess air so that 65% of the carbon burns to CO_2 . Calculate the dew point of the product gas.

Solution

Examine Figure E17.1. To get the dewpoint, a temperature, you have to determine $p_{\text{H}_2\text{O}}^*$. To get $p_{\text{H}_2\text{O}}^*$ you have to calculate $p_{\text{H}_2\text{O}}^* = p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}} p_{\text{Total}}$. The solu-

tion of the problem involves preliminary calculations followed by material balances:

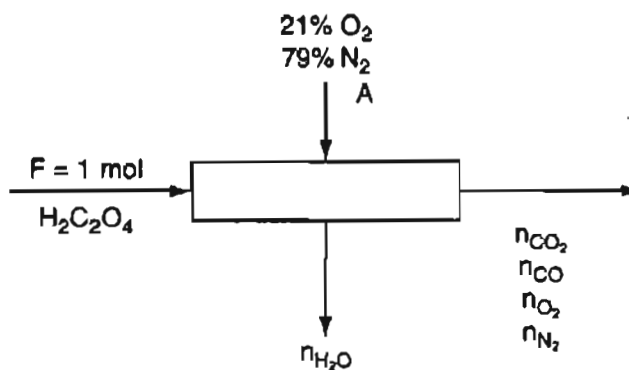


Figure E17.1

1. Calculate the combustion products via material balances.
2. Calculate the mole fraction of the water vapor in the combustion products.
3. Calculate $p_{\text{H}_2\text{O}}$ in the combustion products.
4. Condensation (at constant total pressure) will occur when $p_{\text{H}_2\text{O}}^*$ equals the calculated $p_{\text{H}_2\text{O}}$
5. Look up the temperature corresponding to $p_{\text{H}_2\text{O}}^*$ in the steam tables.

Basis: 1 mol $\text{H}_2\text{C}_2\text{O}_4$

Chemical reaction equations: $\text{H}_2\text{C}_2\text{O}_4 + 0.5 \text{O}_2 \rightarrow 2 \text{CO}_2 + \text{H}_2\text{O}$

$\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO} + \text{H}_2\text{O} + 0.5\text{O}_2$

$$\text{O}_2 \text{ required: } \frac{1 \text{ mol H}_2\text{C}_2\text{O}_4}{1} \times \frac{0.5 \text{ mol O}_2}{1 \text{ mol H}_2\text{C}_2\text{O}_4} = 0.5 \text{ mol O}_2$$

$$\text{Mol O}_2 \text{ entering: } (1 + 2.48)(0.5 \text{ mol O}_2) = 1.74 \text{ mol O}_2$$

Element material balances in moles:

Component	Mol in	Mol out
2H	2	$2 n_{\text{H}_2\text{O}}$
C	2	$n_{\text{CO}} + n_{\text{CO}_2}$
O	$4 + 2(1.74)$	$n_{\text{H}_2\text{O}} + n_{\text{CO}} + 2n_{\text{CO}_2} + 2n_{\text{O}_2}$
2N	$1.74(0.79/0.21)(2)$	$2n_{\text{N}_2}$

With $n_{\text{CO}_2} = (0.65)(2) = 1.30$, the problem has zero degrees of freedom, and the solution of the material balances is

Component	Mol
$n_{\text{H}_2\text{O}}$	1.00
n_{CO_2}	1.30
n_{CO}	0.70
n_{O_2}	1.59
n_{N_2}	6.55
Total	11.14

$$y_{\text{H}_2\text{O}} = 1 \text{ mol H}_2\text{O} / 11.14 \text{ mol total} = 0.0898$$

The partial pressure of the water in the product gas (at an assumed atmospheric pressure) determines the dew point of the stack gas:

$$p_{\text{H}_2\text{O}}^* = y_{\text{H}_2\text{O}} (p_{\text{Total}}) = 0.0898 (101.3 \text{ kPa}) = 9.09 \text{ kPa (1.319 psia)}$$

From steam tables, the dewpoint temperature is: $T = 316.5 \text{ K (43.4}^\circ\text{C or 110}^\circ\text{F)}$.

SELF-ASSESSMENT TEST

Questions

1. What does the term "saturated gas" mean?
2. If a container with a volumetric ratio of air to liquid water of 5 is heated to 60°C and equilibrium is reached, will there still be liquid water present? What about at 125°C ?
3. If a gas is saturated with water vapor, describe the state of the water vapor and the air if it is: (a) heated at constant pressure; (b) cooled at constant pressure; (c) expanded at constant temperature; and (d) compressed at constant temperature.
4. How can you lower the dewpoint of a pollutant gas before analysis?
5. In a gas-vapor mixture, when is the vapor pressure the same as the partial pressure of the vapor in the mixture?
6. Will a noncondensable gas influence the vapor pressure of a vapor as total pressure changes if the temperature remains constant?

Problems

1. The dew point of water in atmospheric air is 82°F . What is the mole fraction of water vapor in the air if the barometric pressure is 750 mm Hg?
2. Ten pounds of KClO_3 is completely decomposed and the oxygen evolved is collected over water at 80°F . The barometer reads 29.7 in. Hg. What weight of saturated oxygen is obtained?
3. Calculate the composition in mol fraction of air that is saturated with water vapor at a total pressure of 100 kPa and 21°C .

4. A benzene–air mixture with the composition between 1.4% and 8.0% can explode if ignited. Will a saturated benzene air mixture at 1 atm be a potential explosive?
5. An 8.00-liter cylinder contains a gas saturated with water vapor at 25.0°C and a pressure of 770 mm Hg. What is the volume of the gas when dry at standard conditions?

Thought Problem

1. Why is it important to know the concentration of water in the air entering a boiler?

17.2 Condensation

From Tom and Ray Magliozzi (*Click and Clack Talk Cars* on PBS):

Question: I have a 1994 Buick LeSabre with 19,000 miles. The car runs perfectly, except after it is parked in our carport. Occasionally, in the morning, I find a water puddle under the exhaust pipe about 6 inches in diameter. There seems to be a black carbon substance on top. It is not greasy and does not seem to be oil. What is this stuff?—Sidney.

Ray: It's good old H_2O , Sidney. Water is one of the byproducts of combustion, so it's produced whenever you run the engine.

Tom: And when you use the car for short trips, the exhaust system never really gets hot enough to evaporate the water so some of it condenses and drips out the end of the tailpipe.

Ray: And since carbon (or “soot”) is also a byproduct of (incomplete) combustion, all exhaust systems have some carbon in them. So the water takes a little bit of carbon with it, and that's what you see on the puddle.

Tom: It's perfectly normal, Sidney. You might even take advantage of it by parking the car with the tailpipe hanging over your perennial bed. That'll save you from watering it a couple of times a week.

Examine the setup for combustion gas analysis shown in Figure 17.1. What error has been made in the setup? If you do not heat the sample of gas collected by the probe and/or put an intermediate condenser before the pump, the analyzer will fill with liquid as the gas sample cools, and will not function.

Condensation is the change of vapor (in a noncondensable gas) to liquid. Some typical ways of condensing a vapor in a gas are:

1. Cool it at constant system total pressure (the volume changes, of course).
2. Cool it at constant total system volume (the pressure changes).
3. Compress it isothermally (the volume changes).

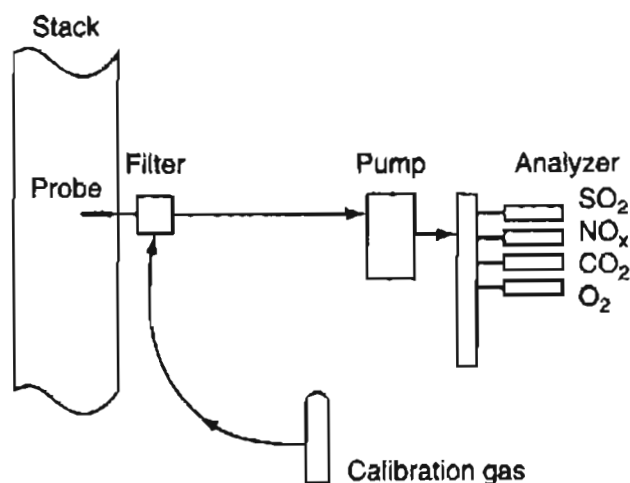


Figure 17.1 Instrumentation for stack gas analysis.

Combinations of the three as well as other processes are possible, of course.

As an example of condensation let's look at cooling a system constant total pressure for a mixture of air and 10% water vapor. Pick the air–water vapor mixture as the system. If the mixture is cooled at constant total pressure from 51°C and 750 mm Hg absolute (point A for the water vapor in Figure 17.2), how low can the temperature go before condensation starts (at point B, the same as point C, in Figure 17.2a, but a different point in Figure 17.2b)? You can cool the mixture until the temperature reaches the dew point associated with the partial pressure of water of

$$p_{\text{H}_2\text{O}}^* \equiv p_{\text{H}_2\text{O}} = 0.10(750) = 75 \text{ mm Hg}$$

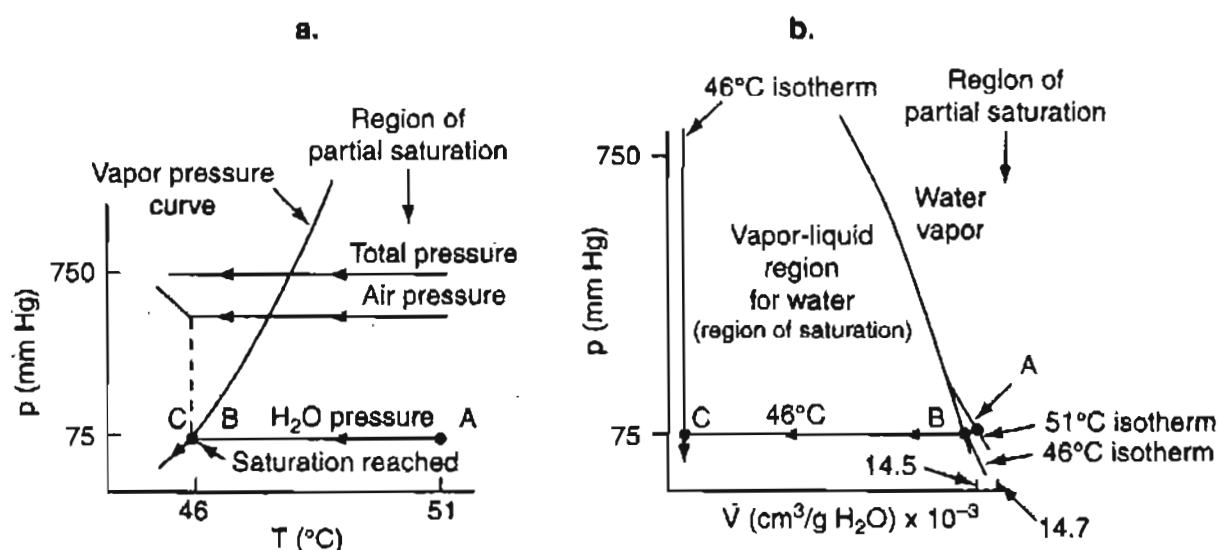


Figure 17.2 Cooling of an air water mixture at constant total pressure. (The lines and curves for the water are distorted for the purpose of illustration—the scales are not arithmetic units.)

From the steam tables you can find that the corresponding temperature is $T = 46^\circ\text{C}$ (points B and C in Figure 17.2a on the vapor pressure curve). After reaching $p^* = 75 \text{ mm Hg}$ at point B, if the condensation process continued, it would continue at constant pressure (75 mm Hg) and constant temperature (46°C) until all of the water vapor had been condensed to liquid (point C in Figure 17.2b). Further cooling would reduce the temperature of the liquid water below 46°C .

If the same air-water mixture starts at 60°C and 750 mm Hg, and is cooled at constant pressure, at what temperature will condensation occur for the same process? Has the dewpoint changed? It is the same because the mole fraction of the water vapor in the air is the same, and $p_{\text{H}_2\text{O}} = 0.10(750) = 75 \text{ mm Hg}$ still. The volume of both the air and the water vapor can be calculated from $pV = nRT$ until condensation starts, at which point the ideal gas law applies only to the residual water vapor, not the liquid. The number of moles of H_2O in the system does not change from the initial number of moles until condensation occurs, at which stage the number of moles of water in the gas phase starts to decrease. The number of moles of air in the system remains constant throughout the process.

Condensation can also occur when the pressure on a vapor-gas mixture is increased. If a pound of saturated air at 75°F is isothermally compressed (with a reduction in volume, of course), liquid water will be deposited out of the air just like water being squeezed out of a wet sponge (see Figure 17.3).

For example, if a pound of saturated air at 75°F and 1 atm (the vapor pressure of water is 0.43 psia at 75°F) is compressed isothermally to 4 atm (58.8 psia), almost three-fourths of the original content of water vapor now will be in the form of liquid, and the air still has a dew point of 75°F . Remove the liquid water, expand the air isothermally back to 1 atm, and you will find that the dew point has been lowered to about 36°F . Here is how to make the calculations. Let 1 = state at 1 atm and 4 = state at 4 atm with $z = 1.00$ for both components.

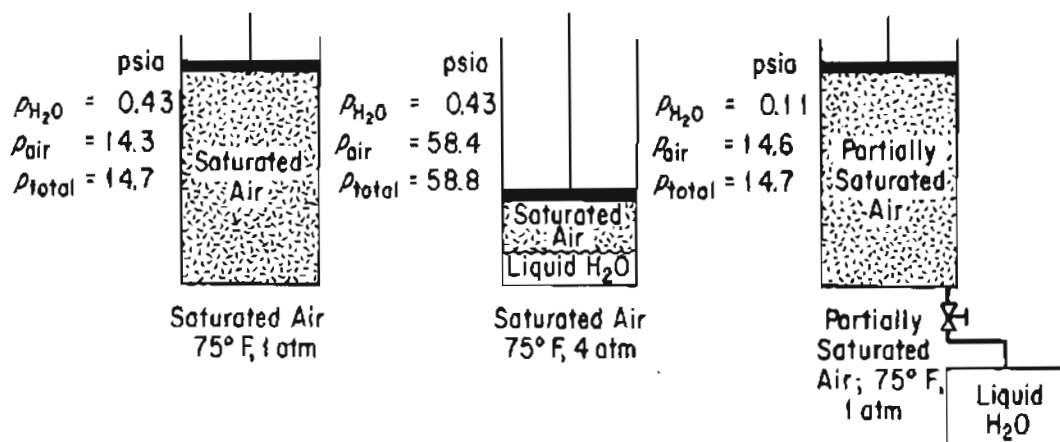


Figure 17.3 Effect of an increase of pressure on saturated air, removal of condensed water, and a return to the initial pressure at constant temperature.

Pick as a basis 0.43 mol of H_2O . For saturated air at 75°F and 4 atm:

$$\left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}}\right)_4 = \left(\frac{p_{\text{H}_2\text{O}}^*}{p_{\text{air}}}\right)_4 = \frac{0.43}{58.4}$$

For the same air saturated at 75°F and 1 atm:

$$\left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}}\right)_1 = \left(\frac{p_{\text{H}_2\text{O}}^*}{p_{\text{air}}}\right)_1 = \frac{0.43}{14.3}$$

Because the moles of air in state 1 and in state 4 are the same, the material balances simplify to

$$\left(\frac{n_4}{n_1}\right)_{\text{H}_2\text{O}} = \frac{\frac{0.43}{58.4}}{\frac{0.43}{14.3}} = \frac{14.3}{58.4} = 0.245$$

that is, 24.5% of the original water will remain as vapor after compression.

After the air–water vapor mixture is returned to a total pressure of 1 atm, to get the partial pressure of the water vapor the following two equations apply at 75°F :

$$\begin{aligned} p_{\text{H}_2\text{O}} + p_{\text{air}} &= 14.7 \\ \frac{p_{\text{H}_2\text{O}}}{p_{\text{air}}} &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}} = \frac{(0.245)(0.43)}{14.7} = 0.00717 \end{aligned}$$

From these two relations you can find that

$$\begin{aligned} p_{\text{H}_2\text{O}} &= 0.105 \text{ psia} \\ p_{\text{air}} &= 14.6 \\ p_{\text{total}} &= 14.7 \text{ psia} \end{aligned}$$

The pressure of the water vapor represents a dew point of about 36°F .

Now let's look at some examples of condensation from a gas–vapor mixture.

EXAMPLE 17.2 Condensation of Benzene from a Vapor Recovery Unit

Emission of volatile organic compounds from processes is closely regulated. Both the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA) have established regulations and standards covering emissions and frequency of exposure. This problem concerns the first step of removal of benzene vapor from an exhaust stream using the process shown in Figure E17.2a. The process has been designed to recover 95% of the benzene from air by compression. What is the exit pressure from the compressor?

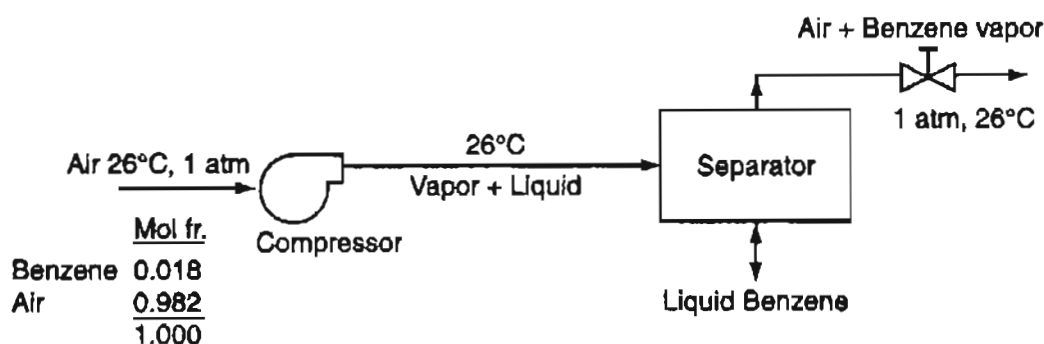


Figure E17.2a

Solution

Figure E17.2b illustrates on a p versus \hat{V} chart for pure benzene what occurs to the benzene vapor during the process. The process is an isothermal compression at 26°C . The partial pressure of the benzene if the entering air at 26°C is less than the saturation pressure. As the total pressure increases, the partial pressure of the benzene reaches the saturation pressure at point A in Figure E17.2b. Subsequently, any increase in total pressure causes the benzene to condense. If you pick the compressor as the system, the compression is isothermal and yields a saturated gas. You can look up the vapor pressure of benzene at 26°C in a handbook or get it from the CD in the back of this book. It is $p^* = 99.7 \text{ mm Hg}$.

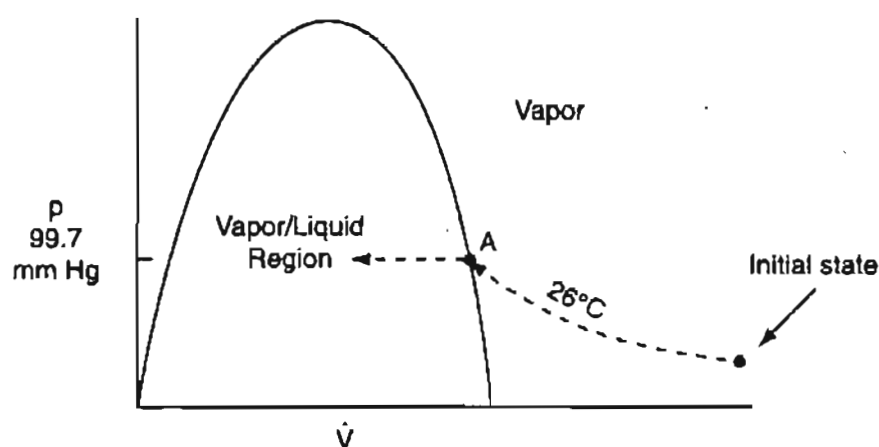


Figure E17.2b

Next you have to carry out a short material balance to determine the outlet concentrations from the compressor:

Basis: 1 g mol entering gas at 26°C and 1 atm

Entering components to the compressor:

$$\begin{aligned}
 \text{mol of benzene} &= 0.018 (1) = 0.018 \text{ g mol} \\
 \text{mol of air} &= 0.982 (1) = \underline{0.982} \text{ g mol} \\
 \text{total gas} &= \quad \quad = 1.000 \text{ g mol}
 \end{aligned}$$

Exiting components in the gas phase from the compressor:

$$\text{mol of benzene} = 0.018 (0.05) = 0.90 \times 10^{-3} \text{ g mol}$$

$$\text{mol of air} = \underline{0.982 \text{ g mol}}$$

$$\text{total gas} = 0.983 \text{ g mol}$$

$$y_{\text{Benzene exiting}} = \frac{0.90 \times 10^{-3}}{0.983} = 0.916 \times 10^{-3} = \frac{p_{\text{Benzene}}}{p_{\text{Total}}}$$

Now the partial pressure of the benzene is 99.7 mm Hg so that

$$p_{\text{Total}} = \frac{99.7 \text{ mm Hg}}{0.916 \times 10^{-3}} = 109 \times 10^3 \text{ mm Hg (143 atm)}$$

Could you increase the pressure at the exit of the compressor above 143 atm? Only if all of the benzene vapor condenses to liquid. Imagine that the dashed line in Figure 17.2b is extended to the left until it reaches the saturated liquid line (bubble point line). Subsequently, the pressure can be increased on the liquid (it would follow a vertical line as liquid benzene is not very compressible).

EXAMPLE 17.3 Smokestack Emissions and Pollution

A local pollution-solutions group has reported the Simtron Co. boiler plant as being an air polluter, and has provided as proof photographs of heavy smokestack emissions on 20 different days. As the chief engineer for the Simtron Co., you know that your plant is not a source of pollution because you burn natural gas (essentially methane), and your boiler plant is operating correctly. Your boss believes the pollution-solutions group has made an error in identifying the stack—it must belong to the company next door that burns coal. Is he correct? Is the pollution-solutions group correct? See Figure E17.3a.



Figure E17.3a

Solution

Methane (CH_4) contains 2 kg mol of H_2 per kilogram mol of C; if you look up the composition of coal in a handbook or on the Internet, you will find that a typical

coal contains 71 kg of C per 5.6 kg of H₂ in 100 kg of coal. The coal analysis is equivalent to

$$\frac{71 \text{ kg C}}{12 \text{ kg C}} \left| \frac{1 \text{ kg mol C}}{12 \text{ kg C}} \right| = 5.92 \text{ kg mol C}$$

$$\frac{5.6 \text{ kg H}_2}{2.016 \text{ kg H}_2} \left| \frac{1 \text{ kg mol H}_2}{2.016 \text{ kg H}_2} \right| = 2.78 \text{ kg mol H}_2$$

or a ratio of $2.78/5.92 = 0.47$ kg mol of H₂/kg mol of C. Suppose that each fuel burns with 40% excess air and that combustion is complete. You can compute the mole fraction of water vapor in each stack gas, and thus get the respective partial pressures of water vapor in the respective flue gases.

Steps 1, 2, 3, and 4

The process is shown in Figure E17.3b.

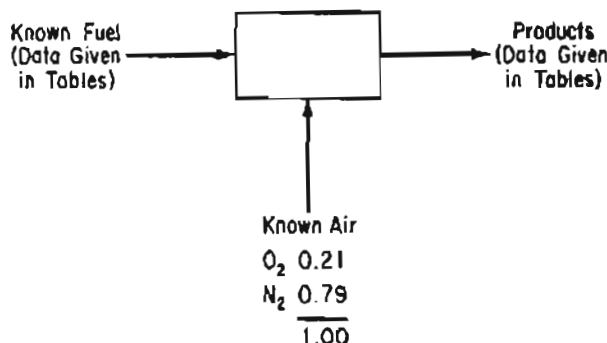
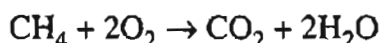


Figure E17.3b

Step 5

Basis: 1 kg mol C

Natural Gas



Step 4

Required O₂: 2

Excess O₂: $2(0.40) = 0.80$ kg mol

N₂: $(2.80)(79/21) = 10.5$ kg mol

Steps 6 and 7

The combustion problem is a standard type of problem having zero degrees of freedom in which both the fuel and air flows are given, and you can calculate the product flows directly, as shown next.

Steps 7, 8, and 9

Tables will make the analysis and calculations compact.

Components	kg mol	Composition of combustion product gases (kg mol)			
		CO ₂	H ₂ O	Excess O ₂	N ₂
C	1.0	1.0			
2H	2.0		2.0		
Air		—	—	0.80	10.5
Total		1.0	2.0	0.80	10.5

The total kilogram moles of gas produced are 14.3 and the mole fraction H₂O is

$$\frac{2.0}{14.3} = 0.14$$

Coal



$$\text{Required O}_2 : \quad 1 + 0.47(1/2) = 1.24 \text{ kg mol}$$

$$\text{Excess O}_2 : \quad (1.24)(0.40) = 0.49 \text{ kg mol}$$

$$\text{N}_2 : \quad 1.40(79/21)[1 + 0.47(1/2)] = 6.50 \text{ kg mol}$$

Components	kg mol	Composition of combustion product gases (kg mol)			
		CO ₂	H ₂ O	Excess O ₂	N ₂
C	1	1			
2H	0.47		0.47		
Air		—	—	0.49	6.5
Total		1	0.47	0.49	6.5

The total kilogram moles of gas produced are 8.46 and the mole fraction H₂O is

$$\frac{0.47}{8.46} = 0.056$$

If the barometric pressure is, say, 100 kPa, and if the stack gas became saturated so that water vapor would start to condense at $p_{\text{H}_2\text{O}}^*$, condensed vapor could be photographed. The respective partial pressures of the water vapor in the combustion gases are:

	Natural gas	Coal
Partial pressure (p^*)	100(0.14) = 14 kPa	100(0.056) = 5.6 kPa
Equivalent temperature:	52.5°C	35°C

Thus, the stack will emit condensed water vapor at higher ambient temperatures for a boiler burning natural gas than for one burning coal. The public, unfortunately, sometimes concludes that all the emissions they perceive are pollution. Natural gas could appear to the public to be a greater pollutant than either oil or coal, whereas, in fact, the emissions are just water vapor. The sulfur content of coal and oil can be released as sulfur dioxide to the atmosphere, and the polluting capacities of mercury and heavy metals in coal and oil are much greater than those of natural gas when all three are being burned properly. The sulfur contents as delivered to the consumers are as follows: natural gas, 4×10^{-4} mol % (as added mercaptans to provide smell for safety); number 6 fuel oil, up to 2.6%; and coal, from 0.5 to 5%. In addition, coal may release particulate matter into the stack plume. By mixing the stack gas with fresh air, and by convective mixing above the stack, the mole fraction water vapor can be reduced, and hence the condensation temperature can be reduced. However, for equivalent dilution, the coal-burning plant will always have a lower condensation temperature.

With the information calculated above, how would you resolve the questions that were originally posed?

EXAMPLE 17.4 Material Balance Involving Condensation

Contamination from accidental discharges of organic compounds used by large industries, airports, small businesses, and homeowners poses a challenging problem for amelioration. Soil contaminated with polyaromatic hydrocarbons can be treated with hot air and steam to drive out the contaminants. If 30.0 m^3 of air at 100°C and 98.6 kPa with a dew point of 30°C is introduced into the contaminated soil, and in the soil the gas cools to 14°C at a pressure of 109.1 kPa , what fraction of the water vapor in the gas at 100°C will condense out in the soil if the gas does not escape too rapidly from the soil?

Solution

Assume the system at 14°C is at equilibrium, and select a fixed volume of initial gas as the system.

Step 5

Basis: $F = 30 \text{ m}^3$ of wet air at 100°C and 98.6 kPa .

Steps 1, 2, 3, and 4

Some of the data has been placed in Figure E17.4

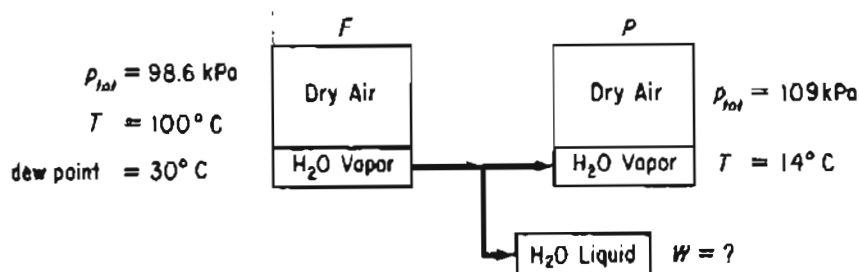


Figure E17.4

In addition, you need to get data for the vapor pressure of water at 30°C and 14°C :

at 30°C $p^* = 4.24 \text{ kPa}$

at 14°C $p^* = 1.60 \text{ kPa}$

By subtracting the vapor pressures from the respective total pressures you can calculate the respective partial pressures of the air, and hence find the compositions of the entering and exiting gas streams. Keep in mind that during the transition from 100°C to 30°C the water vapor does not condense.

The needed compositions are listed below in kPa rather than mole fractions:

Component	F	P
Air:	$98.6 - 4.24 = 94.36$	$109.1 - 1.60 = 107.5$
H ₂ O:	4.24	1.60
Total:	98.6	109.1

Steps 6 and 7

We have two unknowns, P and W , and two independent balances can be made, air and water, thus the degrees of freedom are zero.

Steps 8 and 9

Calculate F (in moles) using the ideal gas law:

$$n = \frac{98.6 \text{ kPa}}{8.314 \text{ (kPa)(m}^3\text{)} / \text{(kg mol)(K)}} \left| \frac{30.0 \text{ m}^3}{373 \text{ K}} \right| = 0.954 \text{ kg mol}$$

The material balances to calculate P and W are

$$\text{Air:} \quad 0.954 \left(\frac{94.36}{98.6} \right) = P \left(\frac{107.50}{109.1} \right)$$

$$\text{H}_2\text{O:} \quad 0.954 \left(\frac{4.24}{98.6} \right) = P \left(\frac{1.60}{109.1} \right) + W$$

$$P = 0.926 \text{ kg mol}$$

$$W = 0.0274 \text{ kg mol}$$

The initial amount of water was

$$0.954 \left(\frac{4.24}{98.6} \right) = 0.0410 \text{ kg mol}$$

and the fraction condensed was

$$\frac{0.0274}{0.0410} = 0.668$$

Step 10

A check can be made using a balance on the total moles:

$$F = P + W \text{ or } 0.954 = 0.926 + 0.0274 \cong 0.953$$

SELF-ASSESSMENT TEST

Questions

1. Can a vapor condense in a gas at temperature T if the partial pressure of the vapor remains less than the vapor pressure of the vapor at T ?
2. Why is substantial excess air used in coal combustion?
3. Is the dew point of a vapor-gas mixture the same variable as the vapor pressure?
4. What and how can variables be changed in a vapor-gas mixture to cause the vapor to condense?
5. Can a gas containing a superheated vapor be made to condense?

Problems

1. A mixture of air and benzene contains 10 mole % benzene at 43°C and 105 kPa pressure. At what temperature can the first liquid form? What is the liquid?
2. Two hundred lb of water out of 1000 lb is electrolytically decomposed into hydrogen and oxygen at 25°C and 740 mm Hg absolute. The hydrogen and oxygen are separated at 740 mm Hg and stored in two different cylinders each at 25°C and a pressure of 5.0 atm absolute. How much water condenses from the gas in each cylinder?
3. Draw a p^* versus T and a p^* versus \hat{V} diagram illustrating the condensation of a superheated vapor from an air-vapor mixture when cooled at constant volume in a vessel until all of the vapor condenses.
4. Repeat Problem #3 for cooling at constant pressure and variable volume.

Thought Problem

1. Water was drained from the bottom of a gasoline tank into a sewer and shortly thereafter a flash fire occurred in the sewer. The operator took special care to make sure that none of the gasoline entered the sewer.

What caused the sewer fire?

Discussion Problems

1. Whenever fossil fuels containing sulfur are burned in heaters or boilers, sulfur dioxide, carbon dioxide, and water vapor are formed analogously, when municipal solid wastes are incinerated HCl and HBr form as well as sulfur dioxide. These acid gases form quite corrosive solutions if the water vapor in the flue gas condenses.

How would you go about estimating the dew point of a flue gas such as one that contained 8% CO_2 , 12% H_2O , 0.73% N_2 , 0.02% SO_2 , 0.015% HCl, 6% O_2 , and 0.01% HBr? What protective measures might be used to avoid corrosion of the heater or stack surfaces? Will the dew point alone be adequate information to alleviate corrosion? Hint: Compounds such as ferric chloride are very hygroscopic even at high temperatures.

2. Expired breath is at body temperature, that is, 37°C , and essentially saturated. Condensation of moisture in respiratory equipment from the expired breath occurs as the breath cools. Such a high humidity level has several implications in developing space suits, diving equipment, oxygen masks in hospitals, and so on. What might they be?

17.3 Vaporization

In June 1992 an explosion near Brenham, Texas, killed three people, injured 19, and caused over \$10 million of damage. Liquid petroleum gas was being pumped into a salt dome for storage under pressure. As the brine (which lay below the liquid petroleum in the salt dome) was forced out by the incoming liquid through a pipe that led to a surface storage pond, apparently too much liquid was forced into the liquid petroleum storage space in the salt dome. The liquid pushed out all of the brine and continued up through the brine discharge line to the surface pond where the liquid vaporized. Apparently a check valve intended to stop such flow failed, and, in addition, someone had turned off the sensor to detect gas at the surface of the pond. After some time the gas cloud reached a source of ignition.

Vaporization is the reverse of condensation, namely the transformation of a liquid into vapor (in a noncondensable gas). You can vaporize a liquid into a noncondensable gas, and raise the partial pressure of the vapor in the gas until the saturation pressure (vapor pressure) is reached at equilibrium. Figure 17.4 shows how the partial pressure of water and air change with time as water evaporates into initially dry

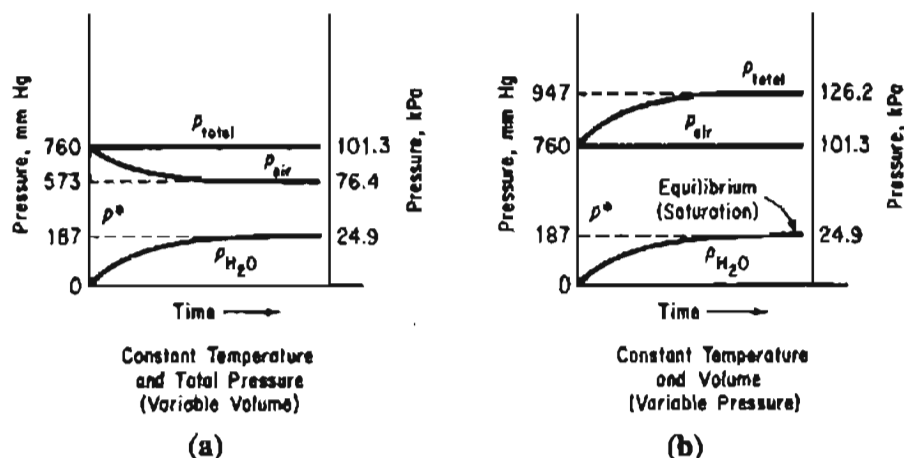


Figure 17.4 Change of partial and total pressure during the vaporization of water into initially dry air: (a) at constant temperature and total pressure (variable volume); (b) at constant temperature and volume (variable pressure).

air. On a p - T diagram, such as Figure 17.2, a liquid would vaporize at the saturation temperature C (the bubble point temperature, which is equal to the dew point temperature) until the air became saturated.

Look at Figure 17.2b, a p - \hat{V} diagram. Evaporation of the liquid would occur from C to B at constant temperature and pressure until the air was saturated. At constant temperature and total pressure, as shown in Figure 17.5, the volume of the air would remain constant, but the volume of water vapor would increase so that the total volume of the mixture would increase.

You might ask: is it possible to have the water evaporate continuously into air and saturate the air, and yet maintain a constant temperature, pressure, and volume, in the cylinder? (*Hint*: What would happen if you let some of the gas-vapor mixture escape from the system?)

You can use Equations (17.1) through (17.3) in solving material balances involved in vaporization problems. For example, if sufficient liquid water is placed in a dry gas that is at 15°C and 754 mm Hg, if the temperature and volume remain constant during the vaporization, what is the final pressure in the system? The partial pressure of the dry gas remains constant because n , V , and T for the dry gas are constant. The water vapor reaches its vapor pressure of 12.8 mm Hg at 15°C . Thus, the total pressure becomes

$$p_{\text{tot}} = p_{\text{H}_2\text{O}} + p_{\text{air}} = 12.8 + 754 = 766.8 \text{ mm Hg}$$

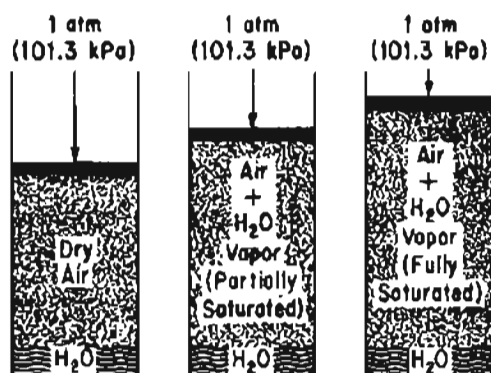


Figure 17.5 Evaporation of water at constant pressure and a temperature of 65°C .

EXAMPLE 17.5 Vaporization to Saturate Dry Air

What is the minimum number of cubic meters of dry air at 20°C and 100 kPa that are necessary to evaporate 6.0 kg of liquid ethyl alcohol if the total pressure remains constant at 100 kPa and the temperature remains 20°C? Assume that the air is blown through the alcohol to evaporate it in such a way that the exit pressure of the air–alcohol mixture is at 100 kPa.

Solution

Look at Figure E17.5. The process is isothermal. The additional data needed are

$$p_{\text{alcohol}}^* \text{ at } 20^\circ\text{C} = 5.93 \text{ kPa}$$

$$\text{Mol. wt. ethyl alcohol} = 46.07$$

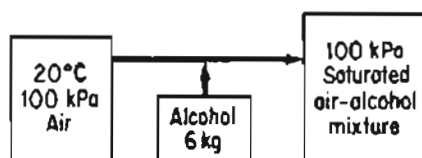


Figure E17.5

The minimum volume of air means that the resulting mixture is saturated; any condition less than saturated would require more air.

Basis: 6.0 kg of alcohol

The ratio of moles of ethyl alcohol to moles of air in the final gaseous mixture is the same as the ratio of the partial pressures of these two substances. Since we know the moles of alcohol, we can find the number of moles of air needed for the vaporization.

$$\frac{p_{\text{alcohol}}^*}{p_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

Once you calculate the number of moles of air, you can apply the ideal gas law. Since $p_{\text{alcohol}}^* = 5.93 \text{ kPa}$

$$p_{\text{air}} = p_{\text{total}} - p_{\text{alcohol}}^* = (100 - 5.93) \text{ kPa} = 94.07 \text{ kPa}$$

$$\frac{6.0 \text{ kg alcohol}}{46.07 \text{ kg alcohol}} \left| \frac{1 \text{ kg mol alcohol}}{1 \text{ kg mol alcohol}} \right| \frac{94.07 \text{ kPa mol air}}{5.93 \text{ kPa mol alcohol}} = 2.07 \text{ kg mol air}$$

$$V_{\text{air}} = \frac{2.07 \text{ kg mol air}}{1} \left| \frac{8.314 \text{ (kPa)(m}^3\text{)}}{(\text{kg mol})(\text{K})} \right| \frac{293 \text{ K}}{100 \text{ kPa}} = 50.4 \text{ m}^3 \text{ at } 20^\circ\text{C and } 100 \text{ kPa}$$

Another way to view this problem is to say that the final volume contains

$V \text{ m}^3$ of alcohol at 5.93 kPa and 20°C

$V \text{ m}^3$ of air at 94.07 kPa and 20°C

$V \text{ m}^3$ of air plus alcohol at 100 kPa and 20°C

Thus, the volume could be calculated from the information about the alcohol using the ideal gas law

$$V_{\text{alcohol}} = \left(\frac{6}{46.07} \right) \left| \frac{8.314}{5.93} \right| \frac{293}{5.93} = 53.5 \text{ m}^3 \text{ at } 20^\circ\text{C and } 5.93 \text{ kPa}$$

The volume of the air is the same but the air is at 94.07 kPa and 20°C.

You can adjust the volume of the alcohol of 53.5 m³ to obtain the volume of the air:

$$V_{\text{air}} = \frac{53.5 \text{ m}^3}{100 \text{ m}^3 \text{ total}} \left| \frac{94.07 \text{ m}^3 \text{ air}}{100 \text{ m}^3 \text{ total}} \right| = 50.3 \text{ m}^3 \text{ of dry air at } 100 \text{ kPa and } 20^\circ\text{C}$$

EXAMPLE 17.6 Vaporization of a Hazardous Component of an Oil Slick

To determine the loss of components from a thin layer of oil spread on water, a 3 mm layer of oil containing various alkanes was allowed to evaporate. It was determined that a simple formula gave good predictions

$$x = x_0 \exp(-Kt)$$

where x = mole fraction of a component at time t

x_0 = initial mole fraction of a component

K = a constant determined by experiment, min^{-1}

It turned out that K could be predicted reasonably well by the relation

$$\log_{10}(p^*) = 1.25 \log_{10}(K) + 0.160$$

where p^* is in atm.

Calculate the half-time (the time required to reduce the concentration of a compound by one-half) of n-heptane in an oil layer 3 mm thick at 22.3°C.

Solution

The vapor pressure of n-heptane at 22.3°C from Perry is 40 mm Hg.

Then

$$\log_{10}\left(\frac{40}{760}\right) = 1.25 \log_{10}(K) + 0.160$$

from which $K = 0.0706 \text{ min}^{-1}$.

$$\ln\left(\frac{x}{x_0}\right) = \ln\left(\frac{0.5}{1}\right) = -Kt = -0.0706t_{1/2}$$

$$t_{1/2} = \frac{-0.693}{-0.0706} = 9.8 \text{ min}$$

Sublimation into a noncondensable gas can occur as well as vaporization.

The Chinook: A Wind That Eats Snow

Each year the area around the Bow River Valley in Southwestern Canada experiences temperatures that go down to -40°F . And almost every year, when the wind called the Chinook blows, the temperature climbs as high as 60°F . In just a matter of a few hours, this Canadian area experiences a temperature increase of about 100°F . How does this happen?

Air over the Pacific Ocean is always moist due to the continual evaporation of the ocean. This moist air travels from the Pacific Ocean to the foot of the Rocky Mountains because air masses tend to move from west to east.

As this moist air mass climbs up the western slopes of the Rocky Mountains, it encounters cooler temperatures, and the water vapor condenses out of the air. Rain falls, and the air mass becomes drier as it loses water in the form of rain. As the air becomes drier, it becomes heavier. The heavier dry air falls down the eastern slope of the Rockies, and the atmospheric pressure on the falling gas increases as the gas approaches the ground.

... the air gets warmer as you increase the pressure. As the air falls down the side of the mountain, its temperature goes up 5.5°F for every thousand-foot drop. So we have warm, heavy, dry air descending upon the Bow River Valley at the base of the Rockies. The Chinook is this warm air (wind) moving down the Rocky Mountains at 50 mph.

Remember, it is now winter in the Bow River Valley, the ground is covered with snow, and it is quite cold (-40°F). Since the wind is warm, the temperature of the Bow River Valley rises very rapidly. Because the wind is very dry, it absorbs water from the melting snow. The word Chinook is an Indian word meaning "snow eater." The Chinook can eat a foot of snow off the ground overnight. The

weather becomes warmer and the snow is cleared away. It's the sort of thing they have fantasies about in Buffalo, New York.

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SELF-ASSESSMENT TEST

Questions

1. If a dry gas is isothermally mixed with a liquid in a fixed volume, will the pressure remain constant with time?
2. If dry gas is placed in contact with a liquid phase under conditions of constant pressure, and allowed to come to equilibrium, will
 - a. the total pressure increase with time?
 - b. the volume of the gas plus liquid plus vapor increase with time?
 - c. the temperature increase with time?
3. If a beaker of water is placed in a bell jar, and the water is maintained at constant temperature while the bell jar is evacuated, what will happen as time goes on?

Problems

1. Carbon disulfide (CS_2) at 20°C has a vapor pressure of 352 mm Hg. Dry air is bubbled through the CS_2 at 20°C until 4.45 lb of CS_2 are evaporated. What was the volume of the dry air required to evaporate this CS_2 (assuming that the air becomes saturated) if the air was initially at 20°C and 10 atm and the final pressure on the air- CS_2 vapor mixture is 750 mm Hg?
2. In an acetone recovery system, the acetone is evaporated into dry N_2 . The mixture of acetone vapor and nitrogen flows through a 2 ft diameter duct at 10 ft/sec. At a sampling point the pressure is 850 mm Hg and the temperature is 100°F . The dew point is 80°F . Calculate the pounds of acetone/hr passing through the duct.
3. Toluene is used as a diluent in lacquer formulae. Its vapor pressure at 30°C is 36.7 mm Hg absolute. If the barometer falls from 780 mm Hg to 740 mm Hg, will there be any change in the volume of dry air required to evaporate 10 kg of toluene?
4. What is the minimum number of m^3 of dry air at 21°C and 101 kPa required to evaporate 10 kg of water at 21°C ?

Thought Problems

1. To reduce problems of condensation associated with continuous monitoring of stack gases, a special probe and flow controller were developed to dilute the flue gas with outside air in a controlled ratio (such as 10 to 1). Does this seem like a sound idea? What

problems might occur with continuous operation of the probe?

2. A large fermentation tank fitted with a 2-in. open vent was sterilized for 30 minutes by blowing in live steam at 35 psia. After the steam supply was shut off, a cold liquid substrate was quickly added to the tank, at which point the tank collapsed inward. What happened to cause the tank to collapse?

Looking Back

In this chapter we explained what saturation means, and showed how the vapor pressure of a compound mixed with a noncondensable gas reaches saturated conditions, which are a function of the temperature and total pressure on the system. Vaporization and condensation problems involving saturation were illustrated via phase diagrams and calculations.

GLOSSARY OF NEW WORDS

Condensation The change of a vapor in a noncondensable gas to liquid.

Evaporation See Vaporization.

Saturated vapor A condensable vapor at its dew point in a noncondensable gas.

Vaporization The transformation of a liquid into a vapor in a noncondensable gas.

SUPPLEMENTARY REFERENCES

In addition to the references in the Frequently Asked Questions in the front material, the following are pertinent.

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Web Sites

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<http://eng.sdsu.edu/testcenter/Test/solv...tems/closed/process/generic.html>

<http://www.netguide.co.nz/condensation>

<http://www.usatoday.com/weather/whumdef.htm>

PROBLEMS

- *17.1 A large chamber contains dry N_2 at 27°C and 101.3 kPa. Water is injected into the chamber. After saturation of the N_2 with water vapor, the temperature in the chamber is 27°C .
- (a) What is the pressure inside the chamber after saturation?
- (b) How many moles of H_2O per mole of N_2 are present in the saturated mixture?
- *17.2 The vapor pressure of hexane (C_6H_{14}) at -20°C is 14.1 mm Hg absolute. Dry air at this temperature is saturated with the vapor under a total pressure of 760 mm Hg. What is the percent excess air for combustion?
- *17.3 Suppose that you place in a volume of dry gas that is in a flexible container a quantity of liquid, and allow the system to come to equilibrium at constant temperature and total pressure. Will the volume of the container increase, decrease or stay the same from the initial conditions? Suppose that the container is of a fixed instead of flexible volume, and the temperature is held constant as the liquid vaporizes. Will the pressure increase, decrease or remain the same in the container?
- *17.4 In a search for new fumigants, chloropicrin (CCl_3NO_2) has been proposed. To be effective, the concentration of chloropicrin vapor must be 2.0% in air. The easiest way to get this concentration is to saturate air with chloropicrin from a container of liquid. Assume that the pressure on the container is 100 kPa. What temperature should be used to achieve the 2.0% concentration? From a handbook, the vapor pressure data are ($T, ^\circ\text{C}$; vapor pressure, mm Hg): 0, 5.7; 10, 10.4; 15, 13.8; 20, 18.3; 25, 23.8; 30, 31.1.

At this temperature and pressure, how many kg of chloropicrin are needed to saturate 100 m^3 of air?

- ✓*17.5 What is the dewpoint of a mixture of air and water vapor at 60°C and 1 atm in which the mole fraction of the air is 12%? The total pressure on the mixture is constant.
- *17.6 Hazards can arise if you do not calculate the pressure in a vessel correctly. One gallon of a hazardous liquid that has a vapor pressure of 13 psia at 80°F is transferred to a tank containing 10 ft^3 of air at 10 psig and 80°F . The pressure seal on the tank containing air will rupture at 30 psia. When the transfer takes place, will you have to worry about the seal rupturing?
- ✓*17.7 A room contains $12,000\text{ ft}^3$ of air at 75°F and 29.7 in Hg absolute. The air has a dew point of 60°F . How many pounds of water vapor are in the air?

- *17.8** One gallon of benzene (C_6H_6) vaporizes in a room that is 20 ft by 20 ft by 9 ft in size at a constant barometric pressure of 750 mm Hg absolute and 70°F. The lower explosive limit for benzene in air is 1.4%. Has this value been exceeded?
- **17.9** A mixture of acetylene (C_2H_2) with an excess of oxygen measured 350 ft³ at 25°C and 745 mm Hg absolute pressure. After explosion the volume of the dry gaseous product was 300 ft³ at 60°C. and the same pressure. Calculate the volume of acetylene and of oxygen in the original mixture. The final gas was saturated. Assume that all of the water resulting from the reaction was in the gas phase after the reaction.
- **17.10** In a science question and answer column, the following question was posed:
On a trip to see the elephant seals in California, we noticed that when the male elephant seals were bellowing, you could see their breath. But we couldn't see our own breath. How come?
- *17.11** One way that safety enters into specifications is to specify the composition of a vapor in air that could burn if ignited. If the range of concentration of benzene in air in which ignition could take place is 1.4 to 8.0 percent, what would be the corresponding temperatures for air saturated with benzene in the vapor space of a storage tank? The total pressure in the vapor space is 100 kPa.
- **17.12** In a dry cleaning establishment warm dry air is blown through a revolving drum in which clothes are tumbled until all of the Stoddard solvent is removed. The solvent may be assumed to be *n*-octane (C_8H_{18}) and have a vapor pressure of 2.36 in. Hg at 120°F. If the air at 120°F becomes saturated with octane, calculate the:
(a) Pounds of air required to evaporate one pound of octane;
(b) Percent octane by volume in the gases leaving the drum;
(c) ft³ of inlet air required per lb of octane. The barometer reads 29.66 in. Hg.
- *17.13** When people are exposed to certain chemicals at relatively low but toxic concentrations, the toxic effects are only experienced after prolonged exposures. Mercury is such a chemical. Chronic exposure to low concentrations of mercury can cause permanent mental deterioration, anorexia, instability, insomnia, pain and numbness in the hands and feet, and several other symptoms. The level of mercury that can cause these symptoms can be present in the atmosphere without a worker being aware of it because such low concentrations of mercury in the air cannot be seen or smelled.

Federal standards based on the toxicity of various chemicals have been set for the "Permissible Exposure Limit," or PEL. These limits are set by the Occupational Safety and Health Administration (OSHA). The PEL is the maximum level of exposure permitted in the workplace based on a time weighted average (TWA) exposure. The TWA exposure is the average concentration permitted for exposure day after day without causing adverse effects. It is based on exposure for 8 hours per day for the worker's lifetime.

The present Federal standard (OSHA/PEL) for exposure to mercury in air is 0.1 mg/m³ as a ceiling value. Workers must be protected from concentrations greater than 0.1 mg/m³ if they are working in areas where mercury is being used.

Mercury manometers are filled and calibrated in a small store room that has no ventilation. Mercury has been spilled in the storeroom and is not completely cleaned

up because the mercury runs into cracks and cracks in the floor covering. What is the maximum mercury concentration that can be reached in the storeroom if the temperature is 20°C? You may assume that the room has no ventilation and that the equilibrium concentration will be reached. Is this level acceptable for worker exposure? Data: $p_{\text{Hg}}^* = 1.729 \times 10^{-4}$ kPa; the barometer reads 99.5 kPa. This problem has been adapted from the problems in the publication *Safety, Health, and Loss Prevention in Chemical Processes* published by the American Institute of Chemical Engineers, New York (1990) with permission.

- *17.14 Figure P17.14 shows a typical *n*-butane loading facility. To prevent explosions either (a) additional butane must be added to the intake lines (a case not shown) to raise the concentration of butane above the upper explosive limit (UEL) of 8.5% butane in air, or (b) air must be added (as shown in the figure) to keep the butane concentration below the lower explosive limit (LEL) of 1.9%. The *n*-butane gas leaving the water seal is at a concentration of 1.5%, and the exit gas is saturated with water (at 20°C). The pressure of the gas leaving the water seal is 120.0 kPa. How many m³ of air per minute at 20.0°C and 100.0 kPa must be drawn through the system by the burner if the joint leakage from a single tank car and two trucks is 300 cm³/min at 20.0°C and 100.0 kPa?

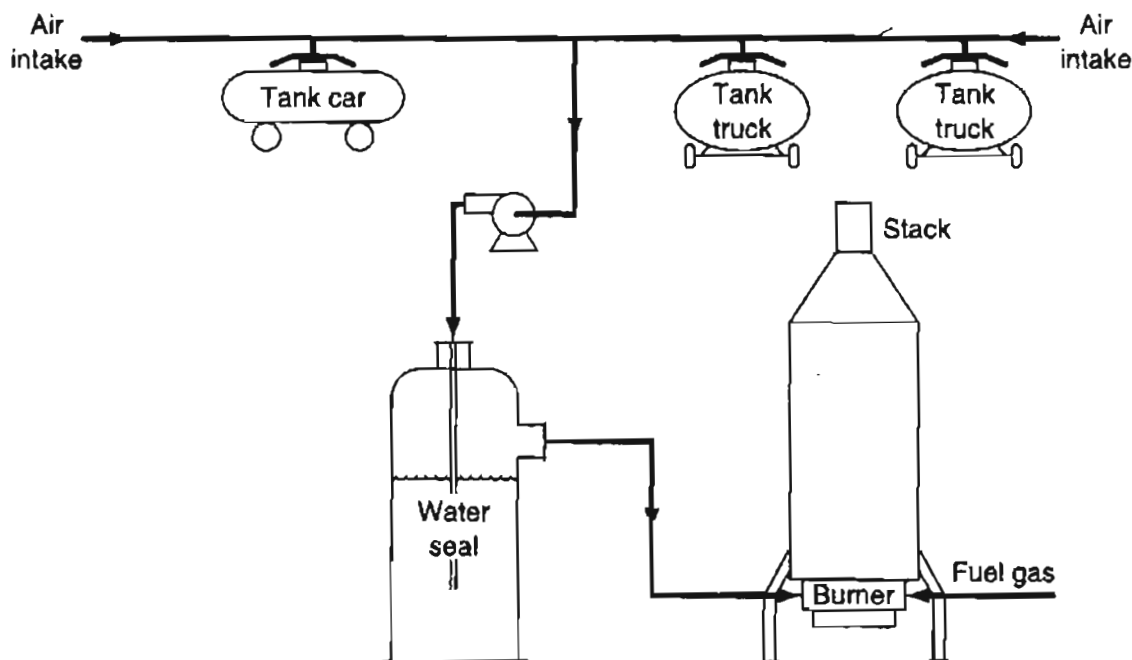


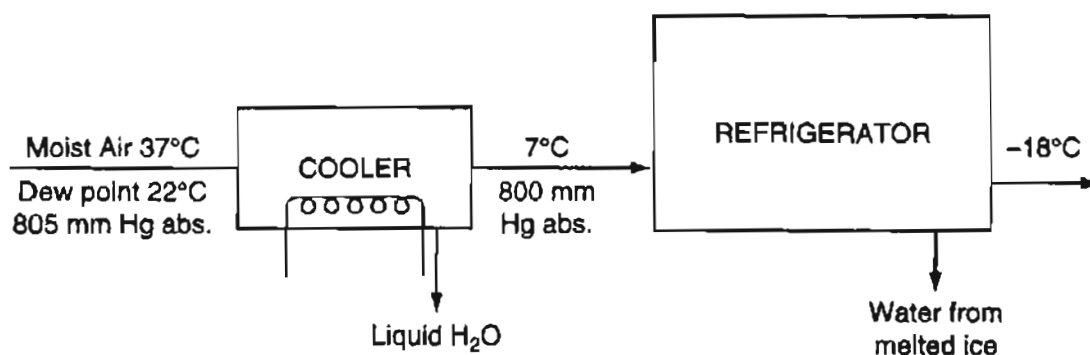
Figure P17.14

- *17.15 When you fill your gas tank or any closed vessel, the air in the tank rapidly becomes saturated with the vapor of the liquid entering the tank. Consequently, as air leaves the tank and is replaced by liquid, you can often smell the fumes of the liquid around the filling vent such as with gasoline.

Suppose that you are filling a closed five-gallon can with benzene at 75°F. After the air is saturated, what will be the moles of benzene per mole of air expelled

from the can? Will this value exceed the OSHA limit for benzene in air (currently 0.1 mg/cm^3)? Should you fill a can in your garage with the door shut in the winter?

- *17.16** All of the water is to be removed from moist air (a process called dehydration) by passing it through silica gel. If $50 \text{ ft}^3/\text{min}$ of air at 29.92 in. Hg absolute with a dew point of 50°F is dehydrated, calculate the pounds of water removed per hour.
- **17.17** Sludge containing mercury is burned in an incinerator. The mercury concentration in the sludge is 0.023% . The resulting gas ($\text{MW} = 32$) is $40,000 \text{ lb/hr}$, at 500°F , and is quenched with water to bring it to a temperature of 150°F . The resulting stream is filtered to remove all particulates. What happens to the mercury? Assume the process pressure is 14.7 psia . (The vapor pressure of Hg at 150°F is 0.005 psia .)
- **17.18** To prevent excessive ice formation on the cooling coils in a refrigerator room, moist air is partially dehydrated and cooled before passing it through the refrigerator room. The moist air from the cooler is passed into the refrigerator room at the rate of $20,000 \text{ ft}^3/24 \text{ hr}$ measured at the entrance temperature and pressure. At the end of 30 days the refrigerator room must be allowed to warm in order to remove the ice from the coils. How many pounds of water are removed from the refrigerator room when the ice on the coils in it melts?



- ✓ ****17.19** Air at 25°C and 100 kPa has a dew point of 16°C . If you want to remove 50% of the initial moisture in the air (at a constant pressure of 100 kPa), to what temperature should you cool the air?
- ✓ ****17.20** One thousand m^3 of air saturated with water vapor at 30°C and 99.0 kPa is cooled to 14°C and compressed to 133 kPa . How many kg of H_2O condense out?
- *17.21** Ethane (C_2H_6) is burned with 20 percent excess air in a furnace operating at a pressure of 100 kPa . Assume complete combustion occurs. Determine the dew-point temperature of the flue gas.
- ✓ *****17.22** Coal as fired contains 2.5% moisture. On the dry basis the coal analysis is C: 80%, H: 6%, O: 8%, ash: 6%. The flue gas analyses CO_2 : 14.0%, CO : 0.4%, O_2 : 5.6%, N_2 : 80.0%. The air used has a dew point of 50°F . The barometer is 29.90 in. Hg . Calculate the dew point of the stack gas.
- ✓ ****17.23** A synthesis gas of the following composition: 4.5% CO_2 , 26.0% CO , 13.0% H_2 , 0.5% CH_4 , and 56.0% N_2 is burned with 10% excess air. The barometer reads 98

kPa. Calculate the dewpoint of the stack gas. To prevent condensation and consequent corrosion, stack gases must be kept well above their dewpoint.

****17.24** CH_4 is completely burned with air. The outlet gases from the burner, which contain no oxygen, are passed through an absorber where some of the water is removed by condensation. The gases leaving the absorber have a nitrogen mole fraction of 0.8335. If the exit gases from the absorber are at 130°F and 20 psia, calculate:

- To what temperature must this gas be cooled at constant pressure in order to start condensing more water?
- To what pressure must this gas be compressed at constant temperature before more condensation will occur?

****17.25** 3M removes benzene from synthetic resin base sandpaper by passing it through a drier where the benzene is evaporated into hot air. The air comes out saturated with benzene at 40°C (104°F). p^* of benzene at 40°C = 181 mm Hg; the barometer = 742 mm Hg. They recover the benzene by cooling to 10°C ($p^* = 45.4$ mm Hg) and compressing to 25 psig. What fraction of the benzene do they recover? The pressure is then reduced to 2 psig, and the air is recycled in the drier. What is the partial pressure of the benzene in the recycled air?

✓ ****17.26** Wet solids containing 40% moisture by weight are dried to 10% moisture content by weight by passing moist air over them at 200°F, 800 mm Hg pressure. The partial pressure of water vapor in the entering air is 10 mm Hg. The exit air has a dew point of 140°F.

How many cubic feet of moist air at 200°F and 800 mm Hg must be used per 100 lb of wet solids entering.

****17.27** Aerobic growth (growth in the presence of air) of a biomass involves the uptake of oxygen and the generation of carbon dioxide. The ratio of the moles of carbon dioxide produced per mole of oxygen consumed is called the respiratory quotient (RQ). Calculate the RQ for yeast cells suspended in the liquid in a well-mixed steady state bioreactor based on the following data:

- Volume occupied by the liquid: 600 m³
- Air (dry) flow rate into the gas (head) space: 600 m³/hr at 120 kPa and 300 K
- Composition of the entering air: 21.0% O₂ and 0.055% CO₂
- Pressure inside the bioreactor: 120 kPa
- Temperature inside the bioreactor: 300 K
- Exit gas: Saturated with water vapor and contains 8.04% O₂ and 12.5% CO₂
- Exit gas pressure: 110 kPa
- Exit gas temperature: 300 K

CHAPTER 18

TWO-PHASE GAS-LIQUID SYSTEMS (PARTIAL SATURATION AND HUMIDITY)

18.1 Terminology Involved for Partial Saturation	538
18.2 Material Balance Problems Involving Partial Saturation	544

Your objectives in studying this chapter are to be able to:

1. Define relative saturation (relative humidity), molal saturation (molal humidity), and humidity by formulas involving the partial pressures of the vapor and the gas.
2. Given the value of the partial saturation in one form, calculate the corresponding values in the other three forms as well as the dew point.
3. Solve material balances involving partial saturation including vaporization and condensation.

Chapter 17 explained partial saturation, but we did not discuss the concept using the terminology commonly encountered by engineers. You need to become acquainted with that terminology and its applications.

Looking Ahead

In this chapter you will again be dealing with partially saturated gases, but this time using some familiar, and some not so familiar, definitions. You will be pleased

to learn that the material balances we treat in processes such as partial saturation, vaporization, condensation, drying, and so on involve no new principles.

18.1 Terminology Involved for Partial Saturation

*We often solve old problems by abandoning them.
Then we go on to create new generations of problems.*

Philip J. David

A while ago partial saturation was involved in an extremely important lawsuit. The lawsuit centered on the way the energy content of natural gas is measured. The price at which producers sell to pipelines and indirectly to consumers is determined by the energy content of the gas, according to the 1978 Natural Gas Policy Act.

Before Congress passed the 1978 law, natural gas was measured as though it were partially saturated with water vapor. The water reduced the energy content of the natural gas per unit volume, and a fixed quantity of water vapor (1.75%) was arbitrarily included in the volumetric measurement regardless of how much water was actually present. Because the actual water vapor content of the gas was rarely as much as 1.75%, and the gas was priced per presumed million Btu in the gas rather than the actual (higher) Btu, the gas producers had to provide more energy per unit volume than they deemed to be fair.

To correct this matter, in 1980 the Federal Energy Regulatory Commission (FERC) decided to change the measurement of natural gas volume so that the water content was no longer assumed to be fixed at 1.75% of the volume of gas, but was instead to be the actual water content. The new ruling enabled the gas producers to charge more for the same volume of natural gas sent to a pipeline. In 1983 a federal appeals court voided the new rule, and furthermore required that gas producers refund an estimated \$1 billion in gas overcharges!

Several ways exist to express the concentration of a vapor in a mixture with a noncondensable gas besides volume percent. In ordinary conversation you will find that the terminology used frequently gets mixed up with the correct terminology. What does the weather person mean when he or she cites the humidity as "60%"? The next time you listen to a weather report check the images and the comments with the following definitions involving partial saturation. When the vapor is water vapor and the gas is air, the special term **humidity** applies. For other gases or vapors, the term saturation is used.

Here are the terms we are going to consider:

- (a) Relative saturation (relative humidity)
- (b) Molal saturation (molal humidity)
- (c) Humidity

18.1-1 Relative Saturation (Relative Humidity)

Relative saturation is defined as the partial pressure of the vapor divided by the vapor pressure of the vapor at the temperature of the gas

$$\mathcal{RS} = \frac{p_{\text{vapor}}}{p^*} = \text{relative saturation} \quad (18.1)$$

where p_{vapor} = partial pressure of the vapor in the gas mixture

p^* = partial pressure of the vapor in the gas mixture if the gas were saturated at the given temperature of the mixture (i.e., the vapor pressure of the vapor component)

Then, for brevity, if the subscript 1 denotes the vapor

$$\mathcal{RS} = \frac{p_1}{p_1^*} = \frac{p_1/p_{\text{tot}}}{p_1^*/p_{\text{tot}}} = \frac{V_1/V_{\text{tot}}}{V_{1,\text{satd}}/V_{\text{tot}}} = \frac{n_1}{n_{1,\text{satd}}} = \frac{\text{mass}_1}{\text{mass}_{1,\text{satd}}} \quad (18.2)$$

You can see that relative saturation, in effect, represents the fractional approach to the total saturation. If you listen to the radio or TV and hear the announcer say that the temperature is 25°C (77°F) and the *relative humidity* is 60%, he or she implies that

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*}(100) = \%RH = 60$$

with both the $p_{\text{H}_2\text{O}}$ and the $p_{\text{H}_2\text{O}}^*$ being measured at 25°C. Zero percent relative saturation means no vapor in the gas. What does 100% relative saturation mean? It means that the partial pressure of the vapor in the gas is the same as the vapor pressure of the substance.

EXAMPLE 18.1 Application of Relative Humidity to Calculate the Dewpoint

The weather report on the radio this morning was that the temperature this afternoon would reach 94°F, the relative humidity would be 43%, the barometer was 29.67 in. Hg, partly cloudy to clear, with the wind from SSE at 8 mi/hr. How many pounds of water vapor would be in 1 mi³ of afternoon air? What would be the dew point of this air?

Solution

The vapor pressure of water at 94°F is 1.61 in. Hg. You can calculate the partial pressure of the water vapor in the air from the given percent relative humidity.

$$p_{\text{H}_2\text{O}} = (1.61 \text{ in Hg})(0.43) = 0.692 \text{ in. Hg}$$

Basis: 1 mi³ water vapor at 94°F and 0.692 in. Hg

$$\frac{1 \text{ mi}^3}{1} \left| \left(\frac{5280 \text{ ft}}{1 \text{ mi}} \right)^3 \right| \frac{492^\circ\text{R}}{555^\circ\text{R}} \left| \frac{0.692 \text{ in. Hg}}{29.92 \text{ in. Hg}} \right| \frac{1 \text{ lb mol}}{359 \text{ ft}^3} \left| \frac{18 \text{ lb H}_2\text{O}}{1 \text{ lb mol}} \right| = 1.51 \times 10^8 \text{ lb H}_2\text{O}$$

Now the dew point is the temperature at which the water vapor in the air will first condense on cooling at *constant pressure and composition*. As the gas is cooled you can see from Equation (18.1) that the relative humidity increases since the partial pressure of the water vapor is constant while the vapor pressure of water decreases with temperature. When the percent relative humidity reaches 100%

$$100 \frac{p_{\text{H}_2\text{O}}}{p^*_{\text{H}_2\text{O}}} = 100\% \quad \text{or} \quad p_{\text{H}_2\text{O}} = p^*_{\text{H}_2\text{O}} = 0.692 \text{ in. Hg}$$

the water vapor will start to condense. From the steam tables you can see that this corresponds to a temperature of about 68–69°F.

18.1-2 Molal Saturation

Another way to express vapor concentration in a gas is to use the ratio of the moles of vapor to the moles of vapor-free gas:

$$\frac{n_{\text{vapor}}}{n_{\text{vapor-free gas}}} = \text{molal saturation} \quad (18.3)$$

If subscripts 1 and 2 represent the vapor and the dry gas, respectively, then for a binary system,

$$\begin{aligned} p_1 + p_2 &= p_{\text{tot}} \\ n_1 + n_2 &= n_{\text{tot}} \\ \frac{n_1}{n_2} &= \frac{p_1}{p_2} = \frac{V_1}{V_2} = \frac{n_1}{n_{\text{tot}} - n_1} = \frac{p_1}{p_{\text{tot}} - p_1} = \frac{V_1}{V_{\text{tot}} - V_1} \end{aligned} \quad (18.4)$$

18.1-3 Humidity (Specific Humidity)

The special term **humidity** (\mathcal{H}) refers to the mass of water vapor per mass of bone-dry air, and is frequently used in connection with the humidity charts that will be described in Chapter 29. By multiplying Equation (18.3) by the appropriate molecular weights, you can find the mass of vapor per mass of dry gas:

$$\mathcal{H} = \frac{(n_{\text{vapor}})(\text{mol. wt. vapor})}{(n_{\text{dry gas}})(\text{mol. wt. dry gas})} = \frac{\text{mass}_{\text{vapor}}}{\text{mass}_{\text{dry gas}}} \quad (18.5)$$

Sometimes you see the word “saturation” used when a vapor other than water is involved. Table 18.1 summarizes the three relations we have discussed.

TABLE 18.1 Summary of the Relationships Used for Vapor–Inert Gas Mixtures

Humidity (normally applied only to water vapor)

$$\mathcal{H} = \frac{\text{mass}_{\text{water vapor}}}{\text{mass}_{\text{dry gas}}} = \frac{(n_{\text{vapor}}) \times (\text{MW}_{\text{vapor}})}{(n_{\text{dry gas}}) \times (\text{MW}_{\text{dry gas}})} = \frac{(p_{\text{vapor}}) \times (\text{MW}_{\text{vapor}})}{(p_{\text{total}} - p_{\text{vapor}}) \times (\text{MW}_{\text{vapor}})}$$

Molal saturation (molal humidity when applied to water vapor)

$$\text{molal saturation} = \frac{n_{\text{vapor}}}{n_{\text{vapor free gas}}} = \frac{n_{\text{vapor}}}{n_{\text{total}} - n_{\text{vapor}}} = \frac{p_{\text{vapor}}}{p_{\text{vapor free gas}}} = \frac{p_{\text{vapor}}}{p_{\text{total}} - p_{\text{vapor}}}$$

Relative saturation (relative humidity when applied to water vapor)

$$RS \text{ (or } \mathcal{RH}) = \frac{p_{\text{vapor}}}{p_{\text{vapor}}^*} = \frac{\frac{p_{\text{vapor}}}{p_{\text{total}}}}{\frac{p_{\text{vapor}}^*}{p_{\text{total}}}} = \frac{n_{\text{vapor}}}{n_{\text{vapor at saturation}}}$$

Now let's look at an example that uses all of the above terms in a problem.

EXAMPLE 18.2 Calculations Involving Various Partial Saturation Terms

The humidity of air at 30°C (86°F) and a total pressure of 750 mm Hg absolute (100 kPa) is 0.0055. Calculate (a) the percent relative humidity, (b) the molal humidity, and (c) the partial pressure of the water vapor in the air. What is the dew point of the air-vapor mixture?

Solution

Data from the steam tables are

$$p_{\text{H}_2\text{O}}^* \text{ at } 30^\circ\text{C} = 1.253 \text{ in. Hg} = 31.8 \text{ mm Hg} = 4.242 \text{ kPa}$$

- (c) To get the partial pressure of the water vapor in the air, start with the value of the humidity of 0.0055 lb water/lb dry air.

$$\mathcal{H} = \frac{(\text{MW}_{\text{H}_2\text{O}})(n_{\text{H}_2\text{O}})}{(\text{MW}_{\text{air}})(n_{\text{air}})} = \frac{(18)(p_{\text{H}_2\text{O}})}{(29)(p_{\text{air}})} = \frac{18(p_{\text{H}_2\text{O}})}{29(p_{\text{total}} - p_{\text{H}_2\text{O}})} = 0.0055$$

from which you can get $p_{\text{H}_2\text{O}} = 6.71 \text{ mm Hg}$.

(a) To get the relative humidity,

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*} = \frac{6.71}{31.8} = 0.21 \text{ or } 21\%$$

(b) The molal humidity is

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{total}} - p_{\text{H}_2\text{O}}} = \frac{6.71}{750 - 6.71} = 9.03 \times 10^{-3}$$

The dew point is the temperature at which the water vapor in the air would first commence to condense when cooled at *constant total pressure*, that is, when the gas becomes completely saturated. This would be at the vapor pressure of 6.7 mm Hg, or about 5.1°C (41°F).

SELF-ASSESSMENT TEST

Questions

1. Write down an equation that expresses the molal saturation in terms of the relative saturation.
2. Write down an equation that expresses the humidity in terms of the relative humidity.
3. Can the value of the relative humidity and the molal saturation ever be equal?
4. At the dew point of an air–water vapor mixture, what are (a) the relative humidity, and (b) the humidity?

Problems

1. A mixture of air and benzene is found to have a 50% relative saturation at 27°C and an absolute pressure of 110 kPa. What is the mole fraction of benzene in the air?
2. A TV announcer says that the dew point is 92°F. If you compress the air to 110°F and 2 psig, what is the percent relative humidity?
3. Nine hundred forty-seven cubic feet of wet air at 70°F and 29.2 in. Hg are dehydrated. If 0.94 lb of H₂O are removed, what was the relative humidity of the wet air?
4. The air in your bedroom is at 20°C and 75% relative humidity. What window temperature will cause water to start condensing on the glass?
5. Toluene is mixed with air at 21°C in such proportions that the partial pressure of the vapor is 10 mm Hg. The total pressure is 745 mm Hg. Calculate the following:
 - a. The relative saturation
 - b. The moles of toluene per mole of vapor-free gas
 - c. The weight of toluene per unit weight of vapor-free gas
 - d. The percentage of toluene by volume

Thought Problems

1. A stirred tank containing liquid CS_2 solvent had to be cleaned because of solid residue that had accumulated on the stirrer. To avoid a possible fire and explosion, the CS_2 was pumped out and the tank blanketed with nitrogen. Then the manhole cover was removed from the top of the tank, and a worker started to remove the solid from the stirrer rod with a scraper. At this point the maintenance worker left for lunch. When he returned to complete the job, a spark caused by the scraper striking the stirrer rod started a flash fire.

How could the fire have occurred despite the preventive measure of using a N_2 blanket?

2. *From:* Marine Board of Investigation
To: Commandant (MVI)
Subj.: SS V. A. *FOGG*, O. N. 244971; sinking with loss of life in Gulf of Mexico on 1 February 1972

Findings of Fact

At 1240 on February 1, 1972, the tankship V. A. *FOGG* departed Freeport, Texas, en route to the Gulf of Mexico to clean cargo tanks that carried benzene residue. The vessel was due to arrive in Galveston, Texas, at 0200, on February 2. At approximately 1545, February 1, the V. A. *FOGG* suffered multiple explosions and sank. All 39 persons aboard died as a result of this casualty. Three bodies were recovered; two of the bodies were identified and one remained unidentified. The other persons were missing and presumed dead.

You are asked your opinion of the most probable cause of the incident. What is your explanation?

Discussion Problem

1. Toward the end of football season, the weather often turns out to be cold, snowy, and rainy. One report from Pittsburgh said that 20 groundskeepers worked around the clock in 18-hour shifts, fighting to prevent snow, gusty winds, and temperatures that dropped below zero from wrecking the delicate artificial playing surface at Three Rivers Stadium.

Although the average football fan considers artificial turf fairly immune from the effects of the elements, at least compared to grass fields, nothing could be further from the truth. Artificial turf can become a carpet of swamp.

To combat the elements, the grounds crew brought a 3-million BTU heating unit and a large propane tank onto the field and situated it beneath the 18-gauge, herculite tarpaulins that cover the field.

After anchoring the tarps with weights and ropes and poles, the crew switched on the heater, blowing the tarps up into a tent of warm air that stood about 15 feet high in the middle of the field and raised the surface temperature to 30 or 35°F. The crew then began a constant vigil to prevent winds from ripping the tarps of the field.

What would the relative humidity be beneath the tarp? Hint: What happens to the combustion products? Would providing a vent to the tarp be better than sealing it to the field from the viewpoint of water removal from the field?

18.2 Material Balance Problems Involving Partial Saturation

Sophisticated smugglers are trying to outwit customs officials who want to prevent the illegal trade in ozone-destroying CFCs. Illegal CFCs, worth an estimated \$300 million a year, are flooding the market, a London seminar on environmental crime was told.

Duncan Brack of the Royal Institute of International Affairs in London outlined some of the techniques smugglers use to pass off illegal CFCs as legal substitutes. One technique, he says, is to hide cylinders of CFCs inside larger cylinders of another gas—the gaseous equivalent of the false-bottomed suitcase. But in many countries, there is no need for smugglers to go to such lengths. For instance, adding nitrogen to cylinders containing illegal CFC-12 raises the pressure in the cylinder to match that used for HCFC-22, a substitute gas that is still legal. A pressure reading is often the only check that is made.

How could you detect the phony CFC? A gas analysis would reveal a vapor in a noncondensable gas, N_2 . Would cooling the contents of a tank reveal an unusual p – T relationship? Most likely. What other suggestions could you make as to detect smugglers of CFC?

In the examples that follow we treat dehydration, humidification, and drying, all processes that involve partial saturation. Keep in mind that if you know the dew point, the relative humidity, the humidity, or any other measure of partial saturation, you can calculate the composition of the air–vapor mixture to use in a material balance.

EXAMPLE 18.3 Dehydration of Moist Air

To avoid deterioration of drugs in a container, you proceed to remove all (0.93 kg) of the H_2O from the moist air in the container that is at 15°C and 98.6 kPa by adsorption in silica gel. The residual dry air measures 1000 m^3 at 20°C and 108.0 kPa. What was the relative humidity of the moist air originally in the container?

Solution

Steps 1, 2, 3, and 4

Figure E18.3 contains the known data.

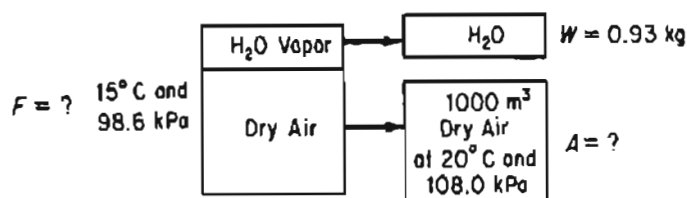


Figure E18.3

Step 5

Either the W or the A stream can serve as the basis. Let's pick

Basis: 1000 m^3 bone-dry air (BDA) at 20°C and 108.0 kPa

Steps 3 and 4

You first need to calculate the amounts (in kg mol) of water vapor and dry air in the original air. $W = 0.93 \text{ kg}$ or

$$\frac{0.93 \text{ kg H}_2\text{O}}{18 \text{ kg H}_2\text{O}} \left| \frac{1 \text{ kg mol H}_2\text{O}}{18 \text{ kg H}_2\text{O}} \right| = 0.0517 \text{ kg mol H}_2\text{O}$$

As for the bone dry air (BDA)

$$\frac{1000 \text{ m}^3 \text{ BDA}}{293 \text{ K}} \left| \frac{273 \text{ K}}{293 \text{ K}} \right| \left| \frac{108.0 \text{ kPa}}{101.3 \text{ kPa}} \right| \left| \frac{1 \text{ kg mol}}{22.4 \text{ m}^3} \right| = 44.35 \text{ kg mol BDA}$$

Steps 6, 7, 8 and 9

The material balances are trivial. All of the water and all of the air in the original moist air are accounted for in the above calculations. The problem has zero degrees of freedom.

To get the relative humidity of the moist air, you first have to calculate the partial pressure of the water vapor in the moist air

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{tot}}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{tot}}} = \frac{0.0517}{0.0517 + 44.35} = 1.164 \times 10^{-3}$$

$$p_{\text{H}_2\text{O}} = (1.164 \times 10^{-3})(108.0) = 0.126 \text{ kPa}$$

Next you look up the vapor pressure at 15°C for water, namely 1.70 kPa . Consequently, the fractional relative humidity of the original air was

$$\frac{0.126}{1.70} = 0.074$$

EXAMPLE 18.4 Humidification of Air

To condition the air in an office building in the winter, 1000 m^3 of moist air per hour at 101 kPa and 22°C with a dew point of 11°C enter the system. The air leaves the system at 98 kPa with a dew point of 58°C . How many kilograms of water vapor are added to each kilogram of wet air entering the process?

Solution**Steps 1, 2, 3, and 4**

The known data appear in Figure E18.4.

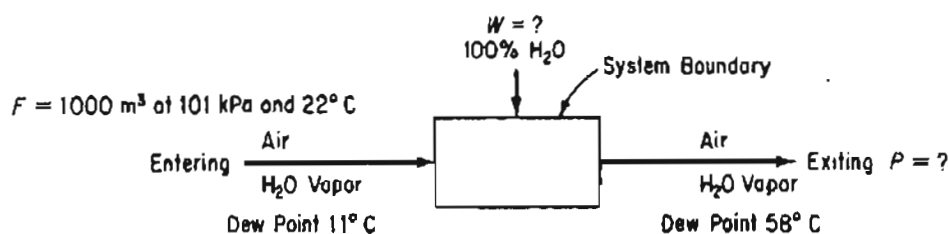


Figure E18.4

The additional vapor pressure data needed are

Dew point temp. ($^{\circ}\text{C}$)	$p^*_{\text{H}_2\text{O}}$ (mm Hg)	$p^*_{\text{H}_2\text{O}}$ (kPa) [†]
11	9.84	1.31
58	136.1	18.14

[†] These values give the partial pressures of the water vapor in the initial and final gas mixtures.

Do you understand that the partial pressures of the water vapor are the pressures at the dew point in each case, and that the dry air has a partial pressure, which is the difference between the total pressure and the partial pressure of the water vapor?

Let the subscript W stand for the water vapor and BDA stand for the dry air.

$$\text{In: } p_{\text{BDA}} = p_{\text{tot}} - p_W = 101 - 1.31 = 99.69 \text{ kPa}$$

$$\text{Out: } p_{\text{BDA}} = 98 - 18.14 = 79.86 \text{ kPa}$$

Step 5

The basis is 1000 m^3 at 101 kPa and 22°C . Other bases could be selected such as 101 kg mol of moist entering air or 98 kg mol of moist exit air.

Step 6 and 7

You have two unknowns, W and P , and can make both an air and a water balance, hence the problem has zero degrees of freedom.

Steps 7, 8, and 9

$$\frac{1000 \text{ m}^3}{101.3 \text{ kPa}} \left| \frac{101 \text{ kPa}}{295 \text{ K}} \right| \frac{273 \text{ K}}{22.4 \text{ m}^3} = 41.19 \text{ kg mol wet air}$$

The material balances are in kg mol:

$$\text{BDA balance: } 41.19 \left(\frac{99.69}{101} \right) = P \left(\frac{79.86}{98} \right)$$

$$P = 49.89 \text{ kg mol}$$

$$\text{Total Balance: } F + W = P$$

$$W = 49.89 - 41.19 = 8.70 \text{ kg mol H}_2\text{O}$$

Step 10

Check using the water balance.

$$\text{Water balance: } 41.19 \left(\frac{1.31}{101} \right) + W = 49.89 \left(\frac{18.1}{98} \right)$$

$$W = 8.68 \text{ kg mol H}_2\text{O ok}$$

Step 9 (Continued)

To calculate the kg of wet air entering

Component	kg mol	Mol. wt.	kg
Dry air	$41.19 \left(\frac{99.69}{101} \right)$	29	1179.0
H ₂ O	$41.19 \left(\frac{1.31}{101} \right)$	18	9.6
Total	41.19		1188.6

$$\text{Water added} = \frac{(8.70)(18)}{1188.6} = 0.132 \frac{\text{kg water}}{\text{kg wet air in}}$$

EXAMPLE 18.5 Condensation of Water from Air

It's a typical late summer Houston day. The temperature is 100°F, the relative humidity is 90%, and the barometer is 29.76 in. Hg. The corner gasoline station is compressing air for its "free air" supply, and compresses the atmospheric air to a pressure of 50 psig, but the work of compression increases the temperature of the compressed air to 120°F. Does water condense out of the air during the compression? If so, how many lb of water per ton of dry air that enters?

Solution**Steps 1 and 2**

Figure E18.5 shows the process and the data.

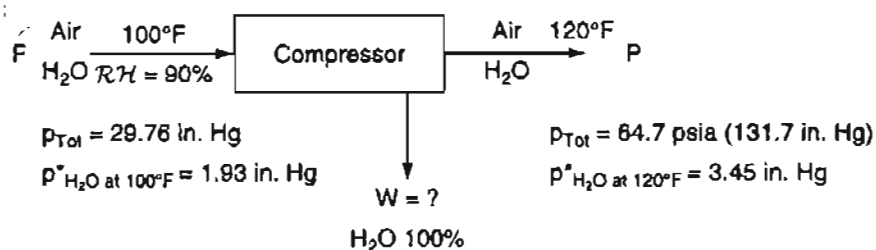


Figure E18.5

Steps 3 and 4

The problem involves making material balances on air and water. To do so, you need to get the compositions of the inlet and outlet streams by first calculating the respective partial pressures of the air and the water vapor.

Inlet Stream F

$$\frac{p_{\text{H}_2\text{O}}}{p^*_{\text{H}_2\text{O}}} = \mathcal{RH} \text{ so that } p_{\text{H}_2\text{O}} = 1.93(0.90) = 1.74 \text{ in. Hg}$$

$$p_{\text{air}} = p_{\text{tot}} - p_{\text{H}_2\text{O}} = 29.76 - 1.74 = 28.02 \text{ in Hg}$$

You can initially assume that condensation takes place, and calculate the partial pressures of the air and water vapor, respectively. You can subsequently check to see if this assumption is false by determining if W is positive or negative. The outlet gas P is saturated when condensation occurs.

Outlet Stream P

$$p_{\text{H}_2\text{O}} = p^*_{\text{H}_2\text{O}} (1.00) = 3.45 \text{ in. Hg}$$

$$p_{\text{air}} = p_{\text{tot}} - p_{\text{H}_2\text{O}} = 131.7 - 3.45 = 128.3 \text{ in. Hg}$$

Step 5

Several bases could be selected: 1 ton of dry air entering, 1 lb of dry air entering, 1 lb mol dry air entering, etc. We will take a somewhat unusual but convenient basis, namely

$$\text{Basis: } F = 29.76 \text{ lb mol}$$

Steps 6 and 7

The number of unknowns is two: P and W . The number of independent balances is two: air and water, hence the degrees of freedom are zero.

Steps 8 and 9

The balances to be used are (note we didn't bother to calculate the mole fraction compositions directly):

$$\text{H}_2\text{O: } \frac{1.74}{29.76}(29.76) = W + P\left(\frac{3.45}{131.7}\right) \quad (\text{a})$$

$$\text{Air: } \frac{28.02}{29.76}(29.76) = 0 + P\left(\frac{128.3}{131.7}\right) \quad (\text{b})$$

The solution to Equations (a) and (b) is

$$P = 28.76 \text{ lb mol } 3 \text{ } W = 0.99 \text{ lb mol}$$

Since W is positive, water condenses during the compression process.

On the basis of 1 ton of dry air

$$\frac{0.99 \text{ lb mol H}_2\text{O out}}{28.02 \text{ lb mol dry air}} \left| \frac{18 \text{ lb water/lb mol water}}{29 \text{ lb air/lb mol air}} \right| \frac{2000 \text{ lb}}{1 \text{ ton}} = 43.9 \text{ lb mol condensed}$$

per ton of dry air. Thus $(43.9)(18.016) = 786 \text{ lb water}$.

SELF-ASSESSMENT TEST

Problems

- ✓1. Gas from a synthetic gas plant analyzes (on a dry basis) 4.8% CO_2 , 0.2% O_2 , 24.4% CO , 0.4% C_2H_4 , 12.2% H_2 , 3.6% CH_4 , and 54.4% N_2 . The coal used analyzes 70.0% C, 6.5% H, 11.0% O, and 12.5% ash. The entering air for combustion has a partial pressure of water equal to 2.67 kPa. The barometer reads 101 kPa. Records show that 465 kg of steam is supplied to the combustion vessel per metric ton of coal fired. Calculate the dew point of the exit gas.
2. A liquid solution of pharmaceutical material to be dried is sprayed into a stream of hot gas. The water evaporated from the solution leaves with the exit gases. The solid is recovered by means of cyclone separators. Operating data are:

Inlet air: 100,000 ft^3/hr , 600°F, 780 mm Hg, humidity of 0.00505 lb $\text{H}_2\text{O}/\text{lb}$ dry air

Inlet solution: 300 lb/hr, 15% solids, 70°F

Outlet air: 200°F, 760 mm Hg, dew point 100°F

Outlet solid: 130°F

Calculate the composition of the outlet solid—it is not entirely dry.

3. A gas leaves a solvent recovery system saturated with benzene at 50°C and 750 mm Hg. The gas analyzes, on a benzene-free basis, 15% CO , 4% O_2 , and the remainder nitrogen. The mixture is compressed to 3 atm and is subsequently cooled to 20°C. Calculate the percent benzene condensed in the process. What is the relative saturation of the final gas?

Thought Problems

1. A company advertises for sale a super efficient two-compartment refrigerator that uses only \$15.00 of electricity per year. They also claim that the food keeps better in it because 100 percent humidity is maintained in the refrigerator. Is it feasible to maintain 100% humidity in a refrigerator?
2. A science question and answer column in response to the question "What produces visible vapor trails behind jets at high altitude" wrote as follows:

Vapor or condensation trails are clouds. When an airplane engine burns jet fuel, water is released into the atmosphere as a byproduct of the combustion. If the air at the high altitude of the airplane is cold and very moist, the water from the engines will cool and condense to form a cloud behind the airplane.

In order to produce a visible condensation trail behind a jet engine, combustion of the jet fuel must take place in an atmosphere with very high relative humidity. The upper level moisture is provided by an incoming low pressure system that pushes moisture ahead of it in an upper level trough.

The presence of condensation trails indicates upper level moisture and signals a system to the west or southwest which could result in precipitation within a day or two. The first precursors to an incoming system are condensation trails aloft and a "halo" around the moon. The halo effect is caused by light passing through the upper atmospheric ice crystals, while vapor trails are caused by the condensation of water in an atmosphere that is very cold and of high relative humidity.

Is the explanation provided by the columnist satisfactory?

- On two different days the temperature and barometric pressure are the same. On day 1 the humidity is high, on day 2 the humidity is low. On which day is the air the most dense? Justify your answer with arguments using Dalton's law and the ideal gas law. Why does the air feel "heavier" on day 1 than on day 2?

Discussion Problem

- The following paper proposed a method for determining moisture loss from biological products. Moisture loss in storage of potatoes, for example, depends on several factors such as species, maturity, harvest conditions, degree of injury, and storage environment. The paper pertained to a method of measuring moisture loss from potatoes based upon measuring the change of moisture content of the air in a closed system containing potatoes. Discuss whether or not the analysis of the method is correct, and what confounding factors might cause it to be in serious error.

The required input data for the calculations were: potato weight in air, jar volume, ambient temperature, barometric pressure, specific gravity, dew-point temperature, time from beginning of test, and the age of the tubers from harvest date. Table 1 lists the variables, their symbols, and their units which were used in the following calculations.

TABLE 1 Symbols and Units of Variables Used in Calculating the Moisture Loss

Symbol	Variable	Symbol	Variable
V_p	Potato tuber volume (cm^3)	T	Ambient air temperature ($^{\circ}\text{F}$)
W_p	Potato weight in air (g)	p_v	Vapor pressure (psia)
SG	Specific gravity (—)	T_d	Dew-point temperature ($^{\circ}\text{F}$)
V_A	Air volume (ft^3)	W	Humidity ratio ($\text{lb}_{\text{H}_2\text{O}}/\text{lb}_{\text{dry air}}$)
V_J	Jar volume (m^3)	W_t	Total weight of vapor in jar (lb)
p	Barometric pressure (in. Hg)	W_{ti}	Initial total weight of vapor at zero time (lb)
p_f	Barometric pressure (psia)	ΔW_a	Difference between initial vapor weight and vapor weight at any particular time (lb)
W_A	Air weight (lb)	ΔW_p	Weight loss per lb of tuber ($\text{lb}_{\text{H}_2\text{O}}/\text{lb}_{\text{tuber}}$)

The volume of the tubers in cubic centimeters was calculated by dividing the potato weight in air by the specific gravity times the density of water (1.0 g/cm^3):

$$V_p = \frac{W_p}{SG} \quad (1)$$

Then, the air volume in cu ft^3 in the jar was determined from the jar volume and the tuber volume:

$$V_A = \frac{(V_J - V_p)}{(2.54 \times 12)^3} \quad (2)$$

The barometric pressure was converted from the readings in inches of mercury to psia

$$p_f = p \left(\frac{14.59}{29.92} \right) (144) \quad (3)$$

The mass of the dry air in the jar was calculated from the ideal gas law equation:

$$W_A = \frac{P_f \times V_A}{53.35(T + 4.60)} \quad (4)$$

The amount of moisture in the air was determined from the dew-point temperature at a particular time and the mass of air in the jar. First, the vapor pressure of the air was calculated from the dew-point temperature, using an equation suggested by Brooker

$$P_v = e^{54.6329 - \frac{12301.688}{T_d + 460}} - 5.16923 \ln (T_d + 460) \quad (5)$$

The mass of the water vapor in the jar was determined from the humidity ratio and the mass of the air in the jar:

$$W = 0.6219 \frac{p_v}{14.696 - p_v} \quad (6)$$

$$W_t = W \times W_A \quad (7)$$

The moisture loss from the tubers was determined from the increase in mass of the water vapor in the jar by subtracting the initial water vapor mass W_{ti} from the water mass W_t at any time greater than zero

$$\Delta W_a = W_t - W_{ti} \quad (8)$$

Then, the weight loss per pound of tuber was determined for the particular time.

$$\Delta W_p = \frac{\Delta W_a}{W_p/454} \quad (9)$$

Looking Back

In this chapter we explained a number of new terms, all of which are used to identify partially saturated conditions in a noncondensable gas. We also solved material balance problems in which these terms were used to get the stream compositions.

GLOSSARY OF NEW WORDS

Humidity The mass of water vapor per mass of bone-dry air.

Molal saturation Moles of vapor divided by the moles of vapor-free gas.

Partial saturation A noncondensable gas containing a vapor whose partial pressure is less than the saturation pressure.

Relative humidity The partial pressure of water vapor in a noncondensable gas divided by the vapor pressure of the water at the temperature of the gas.

Relative saturation The partial pressure of a vapor in a noncondensable gas divided by the saturation pressure of the vapor at the temperature of the gas.

SUPPLEMENTARY REFERENCES

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Instrument Society of America. *Moisture and Humidity*, Instrument Society of America (1985).

Shallcross, D. C. *Handbook of Psychrometric Charts—Humidity Diagrams for Chemical Engineers*, Kluwer Academic, New York (1997).

Web Sites

http://members.aol.com/_ht_a/Rogluthier/humidity.html

<http://w3.one.net/~jwclymer/wet.html>

<http://www.agsci.kvl.dk/~bek/relhum.htm>

<http://www.crh.noaa.gov/mk/soo/docu/humidity.htm>

PROBLEMS

- *18.1 If a gas at 60.0°C and 101.6 kPa abs. has a molal humidity of 0.030, determine:
- the relative humidity
 - the dewpoint of the gas (in °C)

- *18.2 What is the relative humidity of 28.0 m^3 of wet air at 27.0°C that is found to contain 0.636 kg of water vapor?
- *18.3 Air at 80°F and 1 atm has a dew point of 40°F . What is the relative humidity of this air? If the air is compressed to 2 atm and 58°F , what is the relative humidity of the resulting air?
- *18.4 If a gas at 140°F and 30 in. Hg abs. has a molal humidity of $0.03 \text{ mole of H}_2\text{O per mole of dry air}$, calculate:
- The relative humidity (%)
 - The dew point of the gas ($^\circ\text{F}$)
- **18.5 The Weather Bureau reports a temperature of 90°F , a relative humidity of 85% , and a barometric pressure of 14.696 psia .
- What is the molal humidity?
 - What is the humidity (weight basis)?
 - What is the saturation temperature or the dew point?
 - What is the number of degrees of superheat of the water vapor?
 - Determine the molal humidity and dew point if the air is heated to 105°F , the pressure remaining steady.
 - Determine the molal humidity and dew point if the air is cooled to 60°F , the pressure remaining steady.
 - What fraction of the original water is condensed at 60°F ?
- *18.6 The Environmental Protection Agency has promulgated a national ambient air quality standard for hydrocarbons: $160 \mu\text{g}/\text{m}^3$ is the maximum 3-hr concentration not to be exceeded more than once a year. It was arrived at by considering the role of hydrocarbons in the formation of photochemical smog. Suppose that in an exhaust gas benzene vapor is mixed with air at 25°C such that the partial pressure of the benzene vapor is 2.20 mm Hg . The total pressure is 800 mm Hg . Calculate:
- The moles of benzene vapor per mole of gas (total)
 - The moles of benzene per mole of benzene free gas
 - The weight of benzene per unit weight of benzene-free gas
 - The relative saturation
 - The micrograms of benzene per cubic meter
 - The grams of benzene per cubic foot

Does the exhaust gas concentration exceed the national quality standard?

- ✓ **18.7 A constant volume bomb contains air at 66°F and 21.2 psia . One pound of liquid water is introduced into the bomb. The bomb is then heated to a constant temperature of 180°F . After equilibrium is reached, the pressure in the bomb is 33.0 psia . The vapor pressure of water at 180°F is 7.51 psia .
- Did all of the water evaporate?
 - Compute the volume of the bomb in cubic feet.
 - Compute the humidity of the air in the bomb at the final conditions in pounds of water per pound of air.
- *18.8 A mixture of ethyl acetate vapor and air has a relative saturation of 50% at 30°C and a total pressure of 740 mm Hg . Calculate (a) the analysis of the vapor and (b) the molal saturation.

***18.9** In a gas mixture there are 0.0083 lb mol of water vapor per lb mol of dry CH_4 at a temperature of 80°F and a total pressure of 2 atm.

(a) Calculate the relative saturation of this mixture.

(b) Calculate the temperature to which the mixture must be heated in order that the relative saturation becomes 20%.

✓ ****18.10** A drier must remove 200 kg of H_2O per hour from a certain material. Air at 22°C and 50% relative humidity enters the drier and leaves at 72°C and 80% relative humidity. What is the weight (in kg) of bone dry air used per hour? The barometer reads 103.0 kPa.

****18.11** One thousand kg (1 metric ton) of a slurry containing 10% by weight of CaCO_3 are to be filtered in a rotary vacuum filter. The filter cake from the filter contains 60% water. This cake is then placed into a drier and dried to a moisture content of 9.09 kg $\text{H}_2\text{O}/100\text{kg}$ CaCO_3 . If the humidity of the air entering the drier is 0.005 kg of water per kg of dry air and the humidity of the air leaving the drier is 0.015 kg of water per kg of dry air, calculate:

(a) the kg of water removed by the filter

(b) the kg of wet air entering the drier

***18.12** In the manufacture of solid state electronic chips, concern over contamination predominates concern over cost. In the specification of nitrogen, control of the hydrocarbon content is essential. Cryogenic separation is a preliminary stage in the purification process.

If nitrogen gas containing a hydrocarbon at a relative saturation of 3.8% at 750mm Hg absolute and 300K is to be cooled at 750mm Hg to remove 90% of the hydrocarbon as liquid, what must temperature of the outlet gas be? The vapor pressure of the hydrocarbon in the range of interest is given by

$$\ln p^* = 15.9008 - \frac{2788.51}{T - 52.36}$$

where p^* is in mm Hg absolute and T is in K.

***18.13** A wet gas at 30°C and 100.0 kPa with a relative humidity of 75.0% was compressed to 275 kPa, and then cooled to 20°C . How many m^3 of the original gas was compressed if 0.341 kg of condensate (water) was removed from the separator that was connected to the cooler?

***18.14** An absorber receives a mixture of air containing 12 percent carbon disulfide (CS_2). The absorbing solution is benzene, and the gas exits from the absorber with a CS_2 content of 3 percent and a benzene content of 3 percent (because some of the benzene evaporates). What fraction of the CS_2 was recovered?

*****18.15** If a liquid with a fairly high vapor pressure at room conditions is stored in a fixed size tank that breathes, that is, has a vent to the atmosphere, because of ambient temperature changes, how much loss per day occurs in g mol of octane per m^3 of free space under the following conditions, namely the material stored is n -octane at the 50°C during the day and at 10°C at night. The space above the octane consists of air and octane vapor that expands and contracts. Ignore changes in the liquid density.

- **18.16** Thermal pollution is the introduction of waste heat into the environment in such a way as to adversely affect environmental quality. Most thermal pollution results from the discharge of cooling water into the surroundings. It has been suggested that power plants use cooling towers and recycle water rather than dump water into the streams and rivers. In a proposed cooling tower, air enters and passes through baffles over which warm water from the heat exchanger falls. The air enters at a temperature of 80°F and leaves at a temperature of 70°F. The partial pressure of the water vapor in the air entering is 5 mm Hg and the partial pressure of the water vapor in the air leaving the tower is 18 mm Hg. The total pressure is 740 mm Hg. Calculate:
- The relative humidity of the air-water vapor mixture entering and of the mixture leaving the tower
 - The percentage composition by volume of the moist air entering and of that leaving
 - The percentage composition by weight of the moist air entering and of that leaving
 - The percent humidity of the moist air entering and leaving
 - The pounds of water vapor per 1000 ft³ of mixture both entering and leaving
 - The pounds of water vapor per 1000 ft³ of vapor-free air both entering and leaving
 - The weight of water evaporated if 800,000 ft³ of air (at 740 mm and 80°F) enters the cooling tower per day
- *18.17** A drier must evaporate 200 lb/hr of H₂O. Air at 70°F and 50% relative humidity enters the drier, leaving at 140°F and 80% relative humidity. What volume of dry air is necessary per hour?
- *18.18** 1000 ft³ of air, saturated with H₂O, at 30°C and 740 mm Hg, are cooled to a lower temperature and one-half of the H₂O is condensed out. Calculate:
- How many pounds of H₂O are condensed out
 - The volume of dry air at 30°C and 740 mm Hg
- **18.19** Moist air at 25°C and 100 kPa with a dew point of 19.5°C is to be dehydrated so that during its passage through a large cold room used for food storage excess ice formation can be avoided on the chilling coils in the room. Two suggestions have been offered: (1) Cool the moist air to below the saturation temperature at 100 kPa, or (2) compress the moist air above the saturation pressure at 25°C. Calculate the saturation temperature for (1) and the total pressure at saturation for (2).
- If 60% of the initial water in the entering moist air has to be removed before the air enters the cold room, to what temperature should the air in process (1) be cooled?
 - What pressure should the moist air in process (2) reach for the same percent removal?
 - Which process appears to be the most satisfactory? Explain.
- *18.20** A hydrocarbon fuel is burned with bone-dry air in a furnace. The stack gas is at 116 kPa and has a dew point of 47°C. The Orsat analysis of the gas shows 10 mol % carbon dioxide; the balance consists of oxygen and nitrogen. What is the ratio of hydrogen to carbon in the hydrocarbon fuel?
- *18.21** Hot air that is used to dry pharmaceuticals is recycled in a closed loop to prevent the contamination of the moist material from atmospheric impurities. In the first conditioning step for the air, 5000 kg mol/hr at 105 kPa and 42°C with a 90% relative humidity are fed to a condenser to remove some of the water picked up previously in

the process. The air exits the condenser at 17°C and 100 kPa containing 91 kg mol/hr of water vapor. Next, the air is heated in a heat exchanger to 90°C, and then goes to the dryer. By the time the air enters the dryer, the pressure of the stream has dropped to 95 kPa and the temperature is 82°C.

- How many moles of water per hour enter the condenser?
- What is the flow rate of the condensate water in kg/hr?
- What is the dew point of the air in the stream exiting the condenser?
- What is the dew point of the air in the stream entering the dryer?

***18.22** A certain gas contains moisture, and you have to remove the moisture by compression and cooling so that the gas will finally contain not more than 1% moisture (by volume). You decide to cool the final gas down to 21°C.

- Determine the minimum final pressure needed.
- If the cost of the compression equipment is

$$\text{cost in \$} = (\text{pressure in psia})^{1.40}$$

and the cost of the cooling equipment is

$$\text{cost in \$} = (350 - \text{temp. K})^{1.9}$$

is 21°C the best temperature to use?

***18.23** A flue gas from a furnace leaves at 315°C and has an Orsat analysis of 16.7% CO₂, 4.1% O₂, and 79.2% N₂. It is cooled in a spray cooler and passes under slight suction through a duct to an absorption system at 32.0°C to remove CO₂ for the manufacture of dry ice. The gas at the entrance to the absorber analyzes 14.6% CO₂, 6.2% O₂, and 79.2% N₂, due to air leaking into the system. Calculate the cubic meters of air leaked in to the spray cooler per cubic meter of gas to the absorber, both measured at the same temperature and pressure.

***18.24** A wet sewage sludge contains 50% by weight of water. A centrifuging step removes water at a rate of 100 lb/hr. The sludge is dried further by air. Use the data in Figure P18.24 to determine how much moist air (in cubic feet per hour) is required for the process shown.

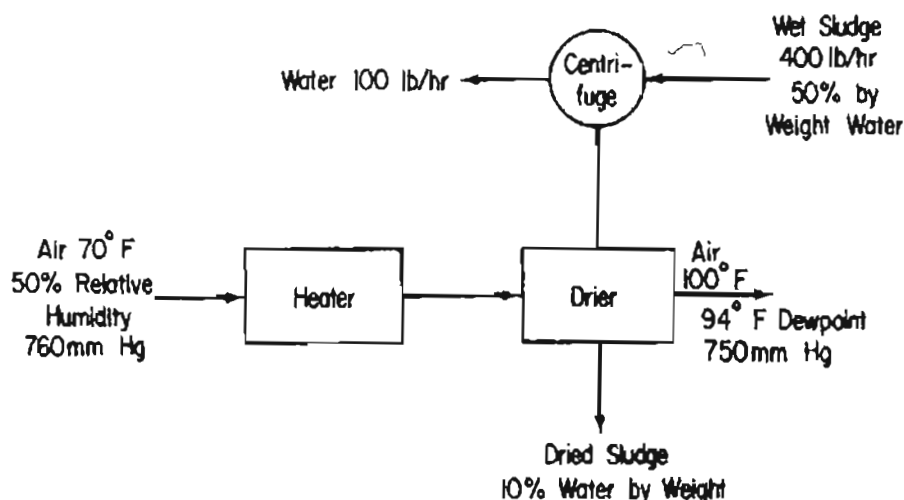


Figure P18.24

- ✓**18.25 To insure a slow rate of drying and thereby prevent checking of the dried product, an inlet relative humidity of 70% at 75°F is specified for the moist air entering the dryer. Outside air is mixed with recycled air from the dryer exit. The air leaving the dryer has a relative humidity of 95% at 70°F. If the outside air has a dewpoint of 40°F, what fraction of the air entering the dryer must come from the outside air and what fraction must come from the recycled air from the dryer exit to provide the desired moisture content in the air fed to the dryer? See Figure P18.25.

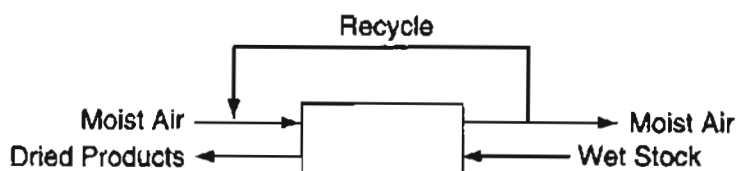


Figure P18.25

- ✓**18.26 A drier must take up 200 lb/hr of H_2O . Entering fresh air at 70°F and 50% RH (F) is mixed with recycle air (R) and enters the drier, leaving at 140°F and 80% RH (P). What is the volume of R (at its conditions) per volume of P (at its conditions)? The barometer reads 14.62 psia, and P and R each are at 0.15 psia gauge pressure. The dew point of the air after the heater is 100°F. See Figure P18.26.

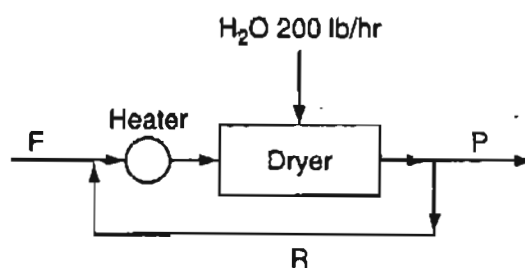


Figure P18.26

- ***18.27 A process is being designed to crystallize a pharmaceutical soap (S) from benzene (Bz) solution. The process is shown in P18.27. A solution of S in Bz is fed to the top of a packed column. Dry air is fed to the bottom of the column. As the liquid passes down, Bz evaporates into the air stream. By the time the liquid leaves the bottom of the column, enough Bz has been removed so that some of the S crystallizes out of solution. Wet crystals of S are then removed in a rotary vacuum filter. The liquor from the filter is mixed with the feed solution and sent to the top of the column. Calculations indicate that the relative saturation of the benzene in the exit air will be 0.70 at 65.0°C.

Answer the following questions:

- Calculate the required feed rate of air, in ft^3/hr at 770 mmHg, 75°C.
- Before developing the final process design, it is necessary to account for the fact that the feed solution really contains 180 ppm of an undesirable toxic material, A, which has the same solubility in Bz as does S. If the present design is put into operation, what will happen to the A? Suggest one (or more) simple modification(s) to the process which will yield crystals of S which contain

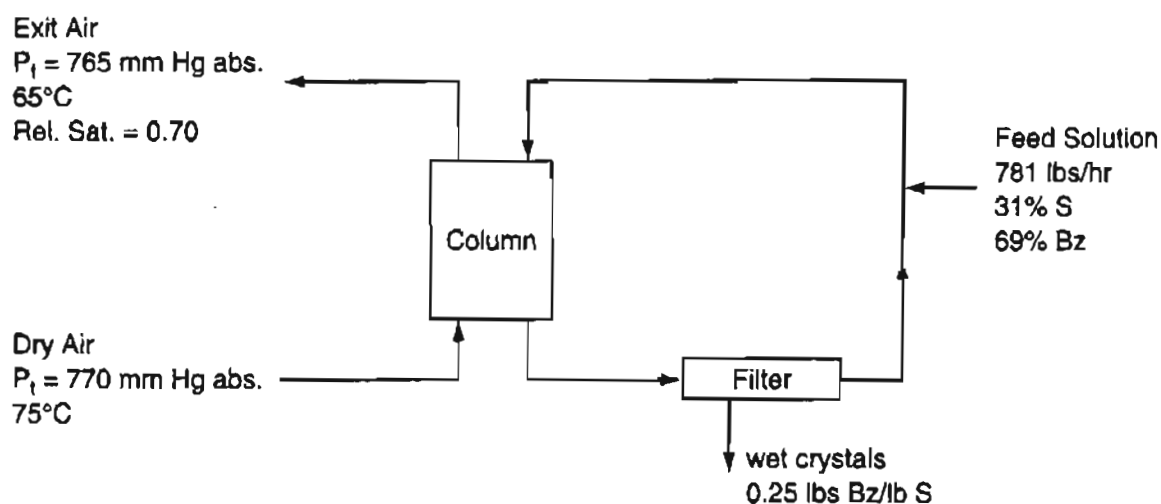


Figure P18.27

much less than 180 ppm of A. For part b of this problem, do not attempt to perform a material balance on the modified process or make any calculations. Just explain qualitatively in a *very few* sentences what happens to the A in the present process, and how the modification will reduce the concentration of A in the product crystals.

- ***18.28 Refer to the process flow diagram (Figure P18.28) for a process that produces maleic anhydride by the partial oxidation of benzene. The moles of O_2 fed to the reactor per mole of pure benzene fed to the reactor is 18.0. The benzene leaves the still at 180°F

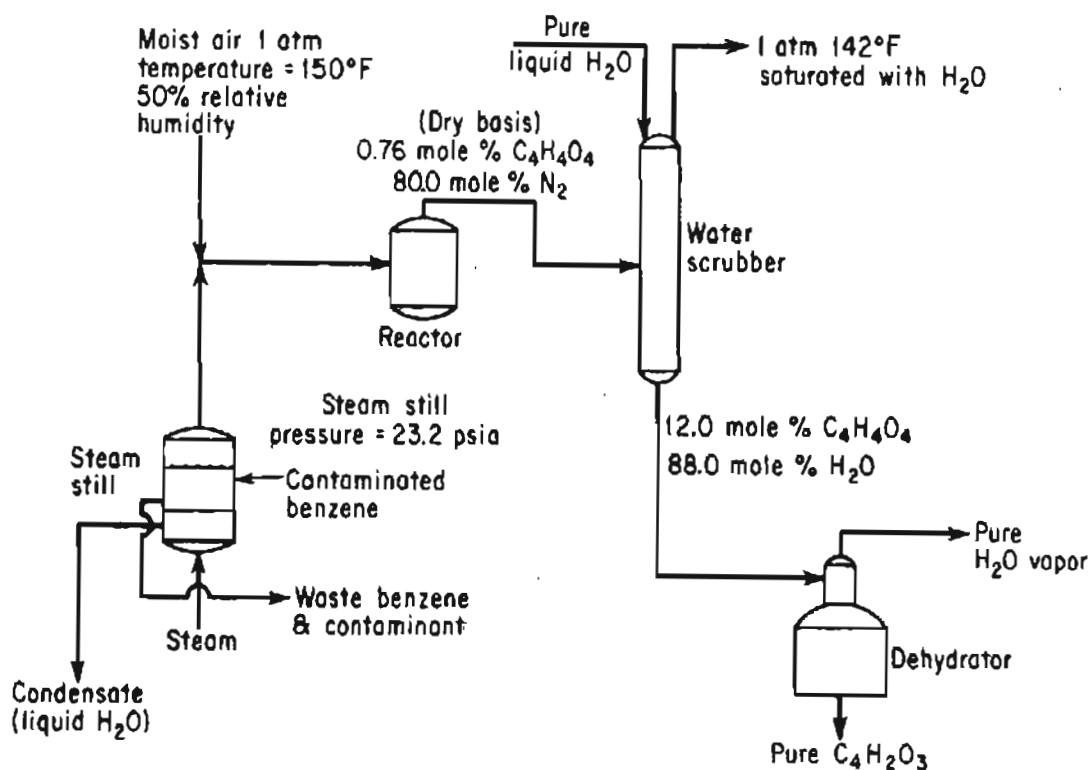
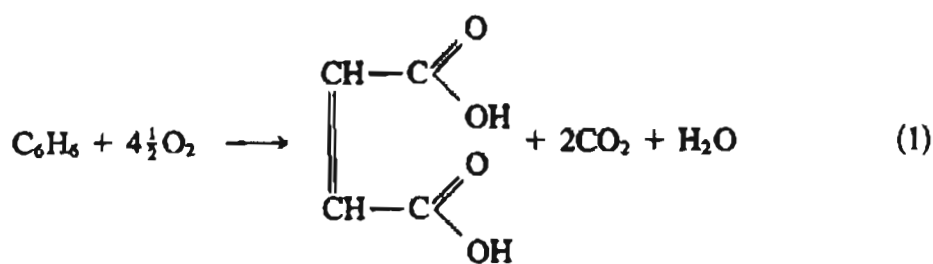


Figure P18.28

before entering the reactor. All of the maleic acid produced in the reactor is removed with water in the bottom stream from the water scrubber. All of the C_6H_6 , O_2 , CO_2 , and N_2 leaving the reactor leave in the stream from the top of the water scrubber, saturated with H_2O . Originally, the benzene contains trace amounts of a nonvolatile contaminant that would inhibit the reaction. This contaminant is removed by steam distillation in the steam still. The steam still contains liquid phases of both benzene and water (benzene is completely insoluble in water). The benzene phase is 80% by weight, and the water phase is 20% by weight of the total of the two liquid phases in the still. Other process conditions are given in the flow sheet. Use the following vapor-pressure data:

Temperature ($^{\circ}F$)	Benzene (psia)	Water (psia)
110	4.045	1.275
120	5.028	1.692
130	6.195	2.223
140	7.570	2.889
150	9.178	3.718
160	11.047	4.741
170	13.205	5.992
180	15.681	7.510
190	18.508	9.339
200	21.715	11.526

The reactions are



Calculate:

- The moles of benzene undergoing reaction (2) per mole of benzene feed to the reactor
- The pounds of H_2O removed in the top stream from the dehydrator per pound mole of benzene feed to the reactor
- The composition (mole percent, wet basis) of the gases leaving the top of the water scrubber
- The pounds of pure liquid H_2O added to the top of the water scrubber per pound mole of benzene feed to the reactor

CHAPTER 19

THE PHASE RULE AND VAPOR-LIQUID EQUILIBRIA

19.1 The Gibbs Phase Rule

561

19.2 Vapor-Liquid Equilibria in Binary Systems

565

Your objectives in studying this chapter are to be able to:

1. Understand and apply the phase rule to systems composed of one or more phases and one or more components.
2. Use Raoult's law and Henry's law to predict the partial pressure of a solvent and a solute, respectively, in the vapor phase.
3. Use the relationship $K_i = y_i/x_i$ to calculate any one of the variables given the other two.
4. Calculate the composition of binary systems at equilibrium for the liquid and vapor phases.

Environmental awareness and associated regulations will require you in the future to evaluate the conflicts that pit producers of fuel, consumers of fuel, governmental agencies, politicians, and environmental activists against each other. If you are going to make wise technical and economic decisions, you have to understand the contents of this chapter.

Looking Ahead

In this chapter we first discuss the Gibbs phase rule that explains the physical degrees of freedom for systems at equilibrium. Then we proceed to take up various relations that you can use to predict the values of p , V , T , and the composition in binary systems at equilibrium.

19.1 The Gibbs Phase Rule

Let us help one another to see things better.

Claude Monet

The phase rule pertains only to systems at equilibrium. **Equilibrium** refers to

- a state of absolute rest
- no tendency to change state
- no processes operating (physical equilibrium)
- no fluxes of energy, mass, or momentum
- no temperature, pressure, or concentration gradients
- no reactions occurring (chemical equilibrium)

Thus, phase equilibrium means that the phases present in a system are invariant, as are the phase properties. By **phase** we mean a part of a system that is *chemically* and *physically* uniform throughout. This definition does not necessarily imply that the phase is continuous. For example, air bubbles in water represent a system that consists of two phases even though the bubbles are a discontinuous phase. The important concept of phase for you to retain is that a gas and liquid at equilibrium can each be treated as having a uniform domain. You can assume that most vapors and liquids at equilibrium are uniform.

The phase rule is concerned only with the **intensive** properties of the system. **By this statement we mean properties that do not depend on the quantity of material present.** If you think about the properties we have employed so far in this book, do you get the impression that pressure and temperature are independent of the amount of material present? Concentration is an intensive variable, but what about volume? The total volume of a system is called an **extensive variable because it does depend on how much material you have. The specific volume and the density, on the other hand, as in cubic meters per kilogram, are intensive properties** because they are independent of the amount of material present. You should remember that the specific (per unit mass or mole) values are intensive properties; the total quantities are extensive properties. Furthermore, the state of a system is specified by the intensive variables, not the extensive ones.

You will find the **Gibb's phase rule** a useful guide in establishing how many intensive properties, such as pressure and temperature, have to be specified to definitely fix all the remaining intensive properties and number of phases that can coexist for any physical system. **The rule can be applied only to systems in equilibrium.** It says that

$$\mathcal{F} = 2 - \mathcal{P} + C \quad (19.1)$$

where \mathcal{F} = number of degrees of freedom (i.e., the number of independent properties that have to be specified to determine all of the intensive properties of each phase of the system of interest)—*not to be confused* with the degrees of freedom calculated in solving material balances that can involve both intensive *and* extensive variables.

\mathcal{P} = number of phases that can exist in the system; a phase is a homogeneous quantity of material such as a gas, a pure liquid, a solution, or a homogeneous solid.

C = number of components (independent chemical species) in the system. Without reaction in the system, the number of components (species) is equal to C . With reaction in the system, the value for C may be reduced to a value less than the number of species, as explained in Appendix L1.

In particular cases additional constraints must be included in Equation (19.1) that reduce the number of degrees of freedom (such as equilibrium and electroneutrality among ions in solution), but we do not have space to discuss them. Refer to the references at the end of this chapter, such as Rao (1985), for details.

Look at Figure 19.1, the three-dimensional representation of the p - \hat{V} - T properties of water that you previously saw in Figure 16.6 in Chapter 16. Consider the vapor phase.

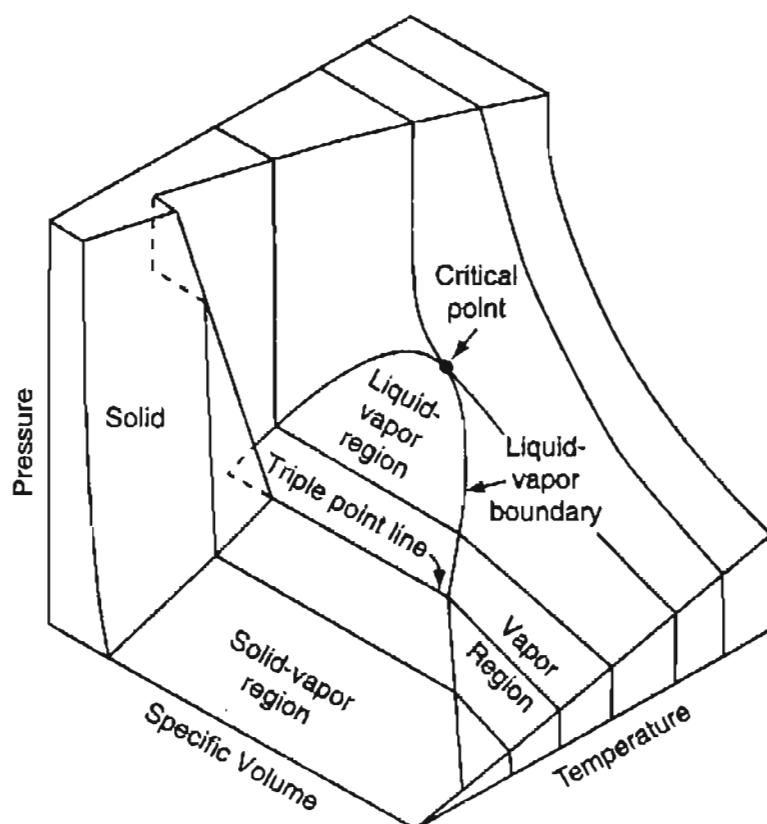


Figure 19.1 Three-dimensional representation of the properties of water shown as a surface with dimensions p , \hat{V} , and T .

You will remember for a pure gas that we had to specify three of the four variables in the ideal gas equation $pV = nRT$ in order to be able to determine the remaining one unknown. You might conclude that $\mathcal{F} = 3$. If we apply the phase rule, for a single phase $\mathcal{P} = 1$, and for a pure gas so that $C = 1$

$$\mathcal{F} = 2 - \mathcal{P} + C = 2 - 1 + 1 = 2 \text{ variables to be specified}$$

How can we reconcile this apparent paradox with our previous statement? Easily! Since the phase rule is concerned with *intensive properties* only, the following are the phase-rule variables to be included in the ideal gas law:

$$\left. \begin{array}{c} p \\ \hat{V}(\text{specific molar volume}) \\ T \end{array} \right\} 3 \text{ intensive properties}$$

Then you can write the ideal gas law as

$$p\hat{V} = RT \quad (19.2)$$

and in this form you can see that by specifying the values of two intensive variables so that $\mathcal{F} = 2$, the third can be calculated. Thus, in the superheated region in the steam tables, you can fix all of the properties of the water vapor by specifying two intensive variables.

An **invariant** system is one in which no variation of conditions is possible without one phase disappearing. In Figure 19.1 the ice–water–water vapor system exists at only one temperature (0.01°C) and pressure (0.611 kPa) along the triple point line (a point in a p - T diagram), and represents one of the invariant states in the water system

$$\mathcal{F} = 2 - \mathcal{P} + C = 2 - 3 + 1 = 0$$

With all three phases present, none of the physical conditions can be varied without the loss of one phase. As a corollary, if the three phases are present, the temperature, the specific volume, and so on, must always be fixed at the same values. This phenomenon is useful in calibrating thermometers and other instruments. Now let's look at some examples of the application of the phase rule.

EXAMPLE 19.1 Applications of the Phase Rule to Systems Without Reaction

Calculate the number of degrees of freedom (how many additional intensive variables must be specified to fix the system) from the phase rule for the following materials at equilibrium:

- (a) Pure liquid benzene
- (b) A mixture of ice and water only
- (c) A mixture of liquid benzene, benzene vapor, and helium gas
- (d) A mixture of salt and water designed to achieve a specific vapor pressure.

What variables might be specified in each case?

Solution

- (a) $N = 1$, $\mathcal{P} = 1$, and $C = 1$, hence $\mathcal{F} = 2 - 1 + 1 = 2$. The temperature and pressure might be specified in the range in which benzene remains a liquid.
- (b) $N = 1$, $\mathcal{P} = 2$, and $C = 1$, hence $\mathcal{F} = 2 - 2 + 1 = 1$. Once either the temperature or the pressure is specified, the other intensive variables are fixed.
- (c) $N = 2$, $\mathcal{P} = 2$, and $C = 2$, hence $\mathcal{F} = 2 - 2 + 2 = 2$. A pair from temperature, pressure, or mole fraction can be specified.
- (d) $N = 2$, $\mathcal{P} = 2$, and $C = 2$, hence $\mathcal{F} = 2 - 2 + 2 = 2$. Since a particular pressure is to be achieved, you would adjust the salt concentration and the temperature of the solution.

Note in (a) and (b) it would be likely that a vapor phase would exist in practice, increasing \mathcal{P} by 1 and reducing \mathcal{F} by one.

EXAMPLE 19.2 Application of the Phase Rule to Systems in which Reactions Can Occur

Calculate the number of degrees of freedom from the phase rule for the following systems at equilibrium

- (a) You have a gas composed of CO , CO_2 , H_2 , H_2O , and CH_4 .
- (b) Sulfur can be removed from high temperature gas streams by a bed of zinc oxide pellets. The results of the decomposition of zinc oxide with carbon show the presence of the following compounds.



Solution

- (a) $\mathcal{P} = 1$, $N = 5$, and you need to determine C . From the information given in Appendix L1, you can determine that the number of independent species is equal to the number of elements present among the compounds, namely 3. Consequently, $C = 3$.

$$\mathcal{F} = 2 - 1 + 3 = 4$$

You might specify T , p , and two mole fractions.

- (b) $\mathcal{P} = 4$ (3 different solid phases plus 1 gas phase). By use of the method explained in Appendix L1, you can calculate that $C = 3$.

$$\mathcal{F} = 2 - 4 + 3 = 1$$

You can fix T or p .

SELF-ASSESSMENT TEST

Questions

- List two intensive and two extensive properties.
- Answer the following questions true or false:
 - A phase is an agglomeration of matter having distinctly identifiable properties such as a distinct refractive index, viscosity, density, X-ray pattern, etc.
 - A solution containing two or more compounds comprises a single phase.
 - A mixture of real gases comprises a single phase.
- Fill in the following table for water

Number of Phases \mathcal{P}	Example	Degrees of Freedom \mathcal{F}	Number of Variables That Can be Adjusted at Equilibrium
1	Steam		
2	Steam and water		
3	Steam, water, and ice		

- Is the critical point a single phase?

Problems

- Determine the number of degrees of freedom from the phase rule for the following systems at equilibrium:
 - Liquid water, water vapor, and nitrogen.
 - Liquid water with dissolved acetone in equilibrium with their vapors.
 - $\text{H}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\ell)$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$, CuSO_4 in solution.
- Can the following system exist at equilibrium: $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{O}(\ell)$, $\text{H}_2\text{O}(\text{g})$, decane(s), decane(l), decane(g)? (*Hint*: Decane is insoluble in water.)

19.2 Vapor–Liquid Equilibria in Binary Systems

In Chapter 16 we discussed vapor–liquid equilibria for a pure component. In Chapters 17 and 18 we covered equilibria of a pure component in the presence of a noncondensable gas. In this section we consider certain aspects of a more general set

of circumstances, namely cases in which equilibrium exists for a binary vapor and liquid system, that is, the vapor and liquid phases each contain both components. Distilling moonshine from a fermented grain mixture is an example of binary vapor–liquid equilibrium in which water and ethanol are the primary components in the system.

The end result of vapor–liquid equilibrium in distillation is that the more volatile component (the component with the higher vapor pressure at a given temperature) tends to accumulate in the vapor phase while the less volatile component tends to accumulate in the liquid phase. Distillation columns, which are used to separate a mixture into its components, are based on this principle. Distillation columns are the most commonly used separation technique in the chemical process industry. A distillation column is comprised of trays that provide contact between liquid and vapor streams inside the column. At each tray, the concentration of the more volatile component is increased in the vapor stream leaving the tray and the concentration of the less volatile component is increased in the liquid leaving the tray. In this manner, applying a number of trays in series, the more volatile component becomes quite concentrated in the overhead stream from the column while the less volatile component becomes concentrated in the bottom product. In order to design and analyze distillation columns, you must be able to quantitatively describe vapor–liquid equilibrium.

When you analyze binary systems at equilibrium, the number of variables involved increases beyond p , T , and \hat{V} . Compositions must be specified, possibly in each phase. It is hard to visualize phase phenomena that should really be portrayed in three or more dimensions. You have to interpret projections of three-dimensional surfaces in two dimensions, such as Figures 19.2 and 19.3 below.

19.2-1 Ideal Solution Relationships

An **ideal solution** is a mixture whose properties such as vapor pressure, specific volume, and so on can be calculated from the knowledge only of the corresponding properties of the pure components and the composition of the solution. For a solution to behave as an ideal solution:

- All of the molecules of all types have roughly the same size.
- All of the molecules have essentially the same intermolecular interactions.

Most solutions are not ideal, but some real solutions are nearly ideal.

a. Raoult's Law The best known relation to make predictions for ideal solutions is **Raoult's Law**:

$$p_i = x_i p_i^*(T) \quad (19.3)$$

where p_i = partial pressure of component i in the vapor phase

x_i = mole fraction of component i in the liquid phase

$p_i^*(T)$ = vapor pressure of component i at T

Figure 19.2 shows how the vapor pressure of the two components in an ideal binary solution sum to the total pressure at 80°C. Compare Figure 19.2, which is based on an ideal solution, with Figure 19.3 which is based on a nonideal solution.

Raoult's law is used primarily for a component whose mole fraction approaches unity (look at methylal in Figure 19.3 as $x_{\text{CS}_2} \rightarrow 0$), or for solutions of components quite similar in chemical nature, such as straight chain hydrocarbons.

b. Henry's Law Henry's law is used primarily for a component whose mole fraction approaches zero, such as a dilute gas dissolved in a liquid:

$$p_i = H_i x_i \quad (19.4)$$

where p_i is the partial pressure in the gas phase of the dilute component at equilibrium at some temperature, and H_i is the *Henry's law constant*. Note that in the limit where $x_i \equiv 0$, $p_i \equiv 0$. Values of H_i can be found in several handbooks and on the Internet. If the solute dissociates into two species such as ions when in solution, Equation (19.4) does not apply.

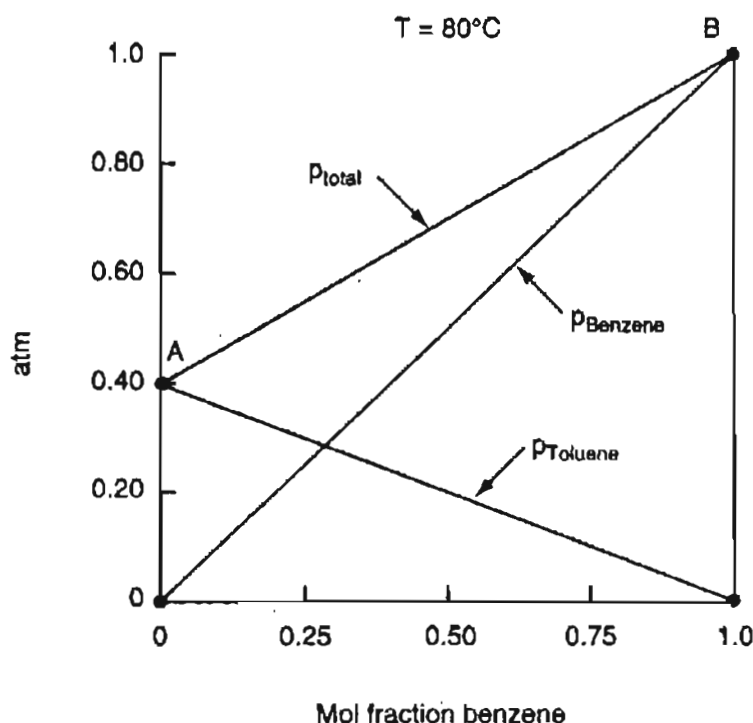


Figure 19.2 Plot of the partial pressures and total pressure as a function of composition calculated using Raoult's law for an ideal solution of benzene and toluene (like species). The vapor pressures of the pure components are shown by points A and B at 0 and 1.0 mole fraction benzene.

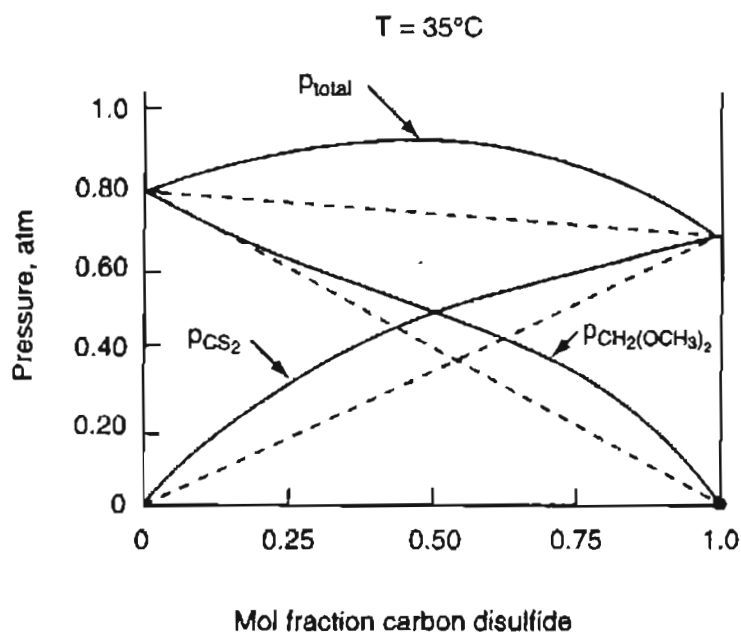


Figure 19.3 Plot of the partial pressures and total pressure (solid lines) exerted by a solution of carbon disulfide (CS₂)–methylal CH₂(OCH₃)₂ as a function of composition. The dashed lines represent the pressures that would exist if the solution were ideal.

Henry's law is quite simple to apply when you want to calculate the partial pressure of a gas in the gas phase that is in equilibrium with the gas dissolved in the liquid phase. Take, for example, CO₂ dissolved in water at 40°C for which the value of H is 69,600 atm/mol fraction. (The large value of H shows that CO₂(g) is only sparingly soluble in water.) If $x_{\text{CO}_2} = 4.2 \times 10^{-6}$, the partial pressure of the CO₂ in the gas phase is

$$p_{\text{CO}_2} = 69,600(4.2 \times 10^{-6}) = 0.29 \text{ atm}$$

From the viewpoint of an aquatic environment, a compound discharged into it will have a low risk potential if it has a large Henry's law constant, and vice-versa. From the viewpoint of an atmospheric environment, a gas with a global warming potential might have less effect if it had a small Henry's law constant.

Even though CO₂ is only slightly soluble, in 1986 the CO₂ buildup in the deep water of Lake Monoun (the "killer lake") in the Cameroon exploded to the surface, causing a 260-foot tidal wave that flattened everything along the shoreline. Also, since CO₂ is denser than air, it blanketed the ground so that 1,750 people and thousands of livestock perished from suffocation or drowning.

Most people would say that when you shake a bottle of soda and see the bubbles form, the pressure in the bottle increases. Certainly if you uncapped the bottle after shaking, the liquid foams out the top. However, if the bottle stays at a fixed temperature, the CO₂ reach an equilibrium state with the liquid, and shaking just displaces some CO₂ from gas phase into the liquid phase, and it is bubbles of this gas (not the dissolved gas) that you see bubble out of the bottle.

19.2-2 Vapor-Liquid Equilibria Phase Diagrams

Adventurers are easier of entrance than exit; and it is but common prudence to see our way out before we venture in.

Aeson

The concept of a phase diagram, which was discussed in Chapter 16, for a pure component can be extended to cover binary mixtures. In this section we treat liquid-vapor equilibria, but you can find information concerning solid-solid, solid-liquid, and solid-vapor equilibria in the references at the end of this chapter. Experimental data usually are presented as pressure as a function of composition at constant temperature, or temperature as a function of composition at a constant pressure. For a pure component, vapor-liquid equilibrium occurs with only one degree of freedom:

$$\mathcal{F} = 2 - \mathcal{P} + C = 2 - 2 + 1 = 1$$

At one atmosphere pressure, vapor-liquid equilibria will occur at only one temperature—the normal boiling point. However, if you have a binary solution, you have two degrees of freedom:

$$\mathcal{F} = 2 - 2 + 2 = 2$$

For a system at a fixed pressure, both the phase compositions and the temperature can be varied over a finite range.

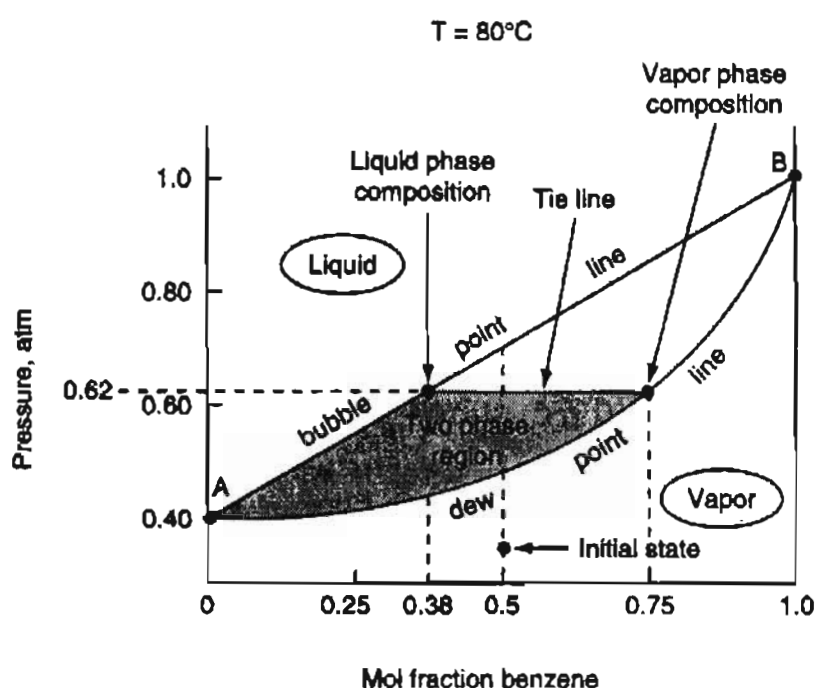


Figure 19.4 Phase diagram for a mixture of benzene and toluene at 80°C . At 0 mol fraction of benzene (point A) the pressure is the vapor pressure of toluene at 80°C . At a mol fraction of benzene of 1 (point B) the pressure is the vapor pressure of benzene at 80°C . The tie line shows the liquid and vapor compositions that are in equilibrium at a pressure of 0.62 atm (and 80°C).

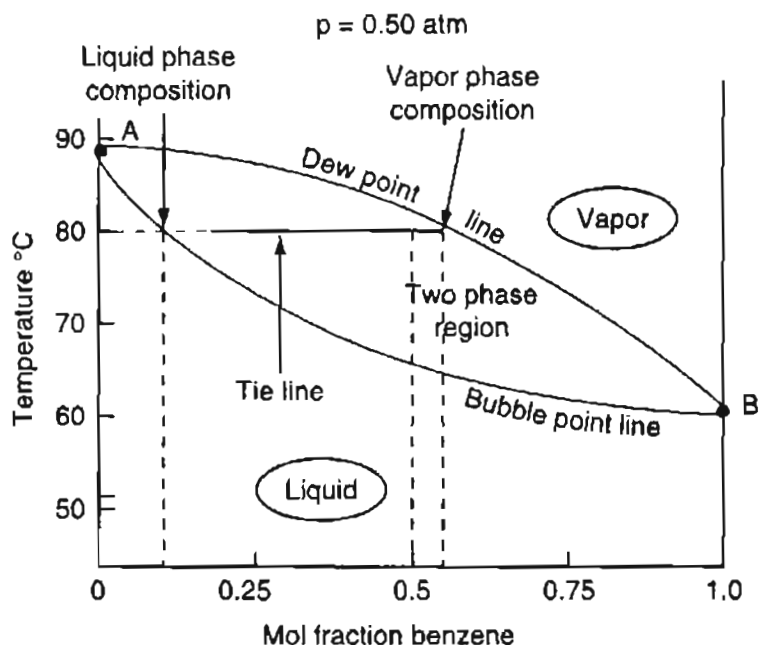


Figure 19.5 Phase diagram for a mixture of benzene and toluene at 0.50 atm. At 0 mole fraction of benzene (point A), the temperature corresponds to the vapor pressure of toluene of 0.50 atm. At a mol fraction of benzene of 1 (point B), the temperature corresponds to the vapor pressure of benzene of 0.50 atm. The tie line shows the respective liquid and vapor compositions that are in equilibrium at a temperature of 80°C (and 0.50 atm) for an initial mixture of 50% benzene and 50% toluene.

Figures 19.4 and 19.5 show the vapor–liquid envelope for a binary mixture of benzene and toluene, which is essentially ideal.

You can interpret the information on the phase diagrams as follows. Suppose you start in Figure 19.4 at a 50–50 mixture of benzene–toluene at 80°C and 0.30 atm in the vapor phase. Then you increase the pressure on the system until you reach the dew point at about 0.47 atm, at which point the vapor starts to condense. At 0.62 atm the mol fraction of the benzene in the vapor phase will be about 0.75 and the mol fraction in the liquid phase will be about 0.38, as indicated by the tie line. As you increase the pressure from 0.62 to about 0.70 atm, all of the vapor will be condensed to liquid. What will the composition of the liquid be? 0.50 benzene, of course! Can you carry out an analogous conversion of vapor to liquid using Figure 19.5, the temperature–composition diagram?

Phase diagrams for nonideal solutions abound. Figure 19.6 shows the temperature–composition diagram for isopropanol in water at 1 atm. Note the minimum boiling point at a mole fraction of isopropanol of about 0.68, a point called an **azeotrope** (a point for which the dew point curve and the bubble point curve coincide) that makes separation by distillation different.

19.2-3 K-Value (Vapor–Liquid Equilibrium Ratio)

For nonideal as well as ideal mixtures that comprise two (or more) phases, it proves to be convenient to express the ratio of the mole fraction in one phase to the mole fraction of the same component in another phase in terms of a **distribution coefficient** or **equilibrium ratio K**, usually called a **K-value**. For example.

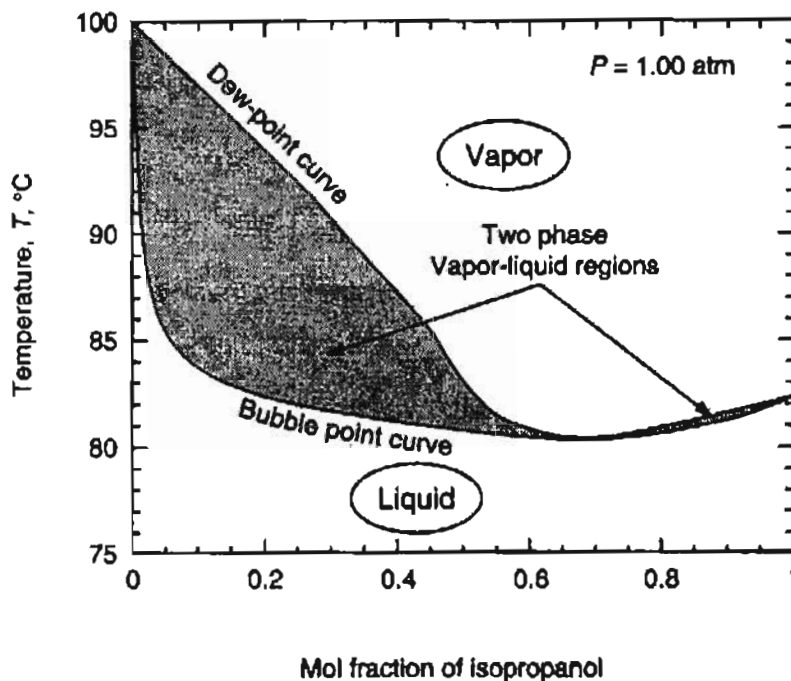


Figure 19.6 Phase diagram for a nonideal mixture of isopropanol and water at 1 atm.

$$\text{Vapor-liquid: } \frac{y_i}{x_i} = K_i \quad (19.5a)$$

$$\text{Liquid-liquid: } \frac{x_{1i}}{x_{2i}} = K_{Li} \quad (19.5b)$$

and so on. Refer to Chapter 20 for soil sorption coefficients. If the ideal gas law (Dalton's law), $p_i = y_i p_{\text{total}}$, applies to the gas phase, and the ideal Raoult's law applies to the liquid phase, $p_i = x_i p_i^*(T)$, then for the ideal system

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*(T)}{p_{\text{Total}}} \quad (19.5c)$$

Equation (19.5c) gives reasonable estimates of K_i values at low pressures for components well below their critical temperatures, but yields values too large for components above their critical temperatures, at high pressures, and/or for polar compounds. For nonideal mixtures Equation (19.5a) can be employed if K_i is made a function of temperature, pressure, and composition so that relations for K_i can be fit by experimental data and used directly, or in the form of charts, for design calculations, as explained in some of the references at the end of this chapter. Figure 19.7 shows how K varies for the nonideal mixture of acetone and water at 1 atm. K can be greater or less than one but never negative.

For ideal solutions you can calculate values of K using Equation (19.5c). For nonideal solutions you can get approximate K values from

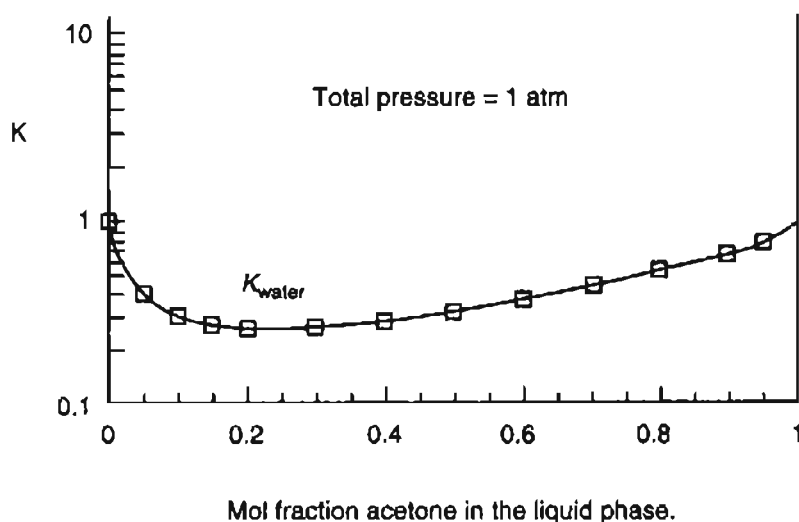


Figure 19.7 Change of K of water with composition at $p = 1$ atm.

1. Empirical equations such as*

$$\text{If } T_{c,i}/T > 1.2: \quad K_i = \frac{(p_{c,i}) \exp [7.224 - 7.534/T_{r,i} - 2.598 \ln T_{r,i}]}{p_{\text{total}}}$$

2. Databases (refer to the supplementary references at the end of the chapter).
3. Charts such as Figure 19.8.
4. Thermodynamic relations (refer to the references at the end of the chapter).

Typical problems you should be able to solve that involve the use of the equilibrium coefficient K_i together with material balances are:

1. Calculate the bubble point temperature of a liquid mixture given the total pressure and liquid composition.
2. Calculate the dew point temperature of a vapor mixture given the total pressure and vapor composition.
3. Calculate the composition of the vapor and liquid streams, and their respective quantities, when a liquid of given composition is partially vaporized (**flashed**) at a given temperature and pressure (the temperature must lie between the bubble and dew point temperatures of the feed).
4. Calculate the related equilibrium vapor–liquid compositions over the range of mole fractions from 0 to 1 as a function of temperature given the total pressure.

Analogous problems occur with respect to calculating the total pressure given a fixed temperature.

Let's next outline the procedure to solve the first three problems cited above.

*S.I. Sandler, in *Foundations of Computer Aided Design*, Vol. 2, R.H.S. Mah and W.D. Seider, eds., p. 83, American Institute of Chemical Engineers, New York (1981).

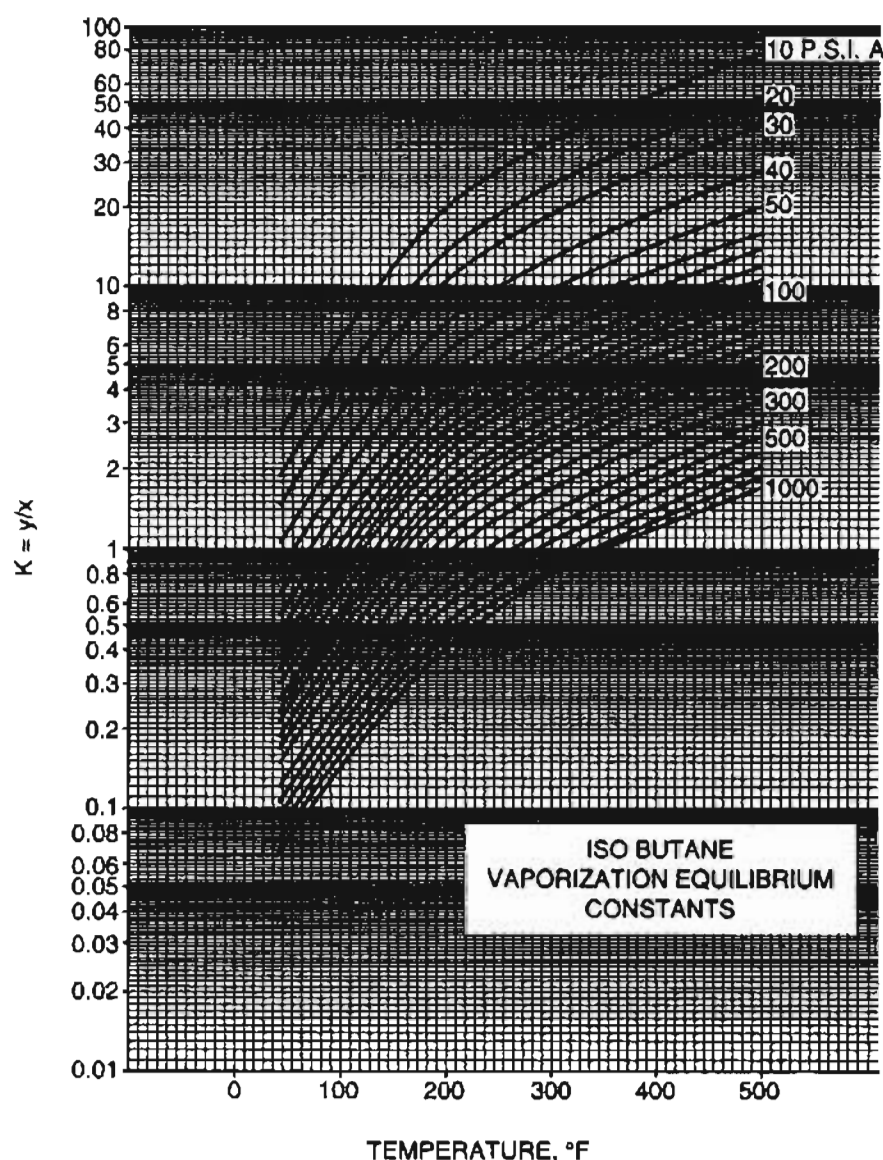


Figure 19.8 K -values for isobutane as a function of temperature and pressure. From Natural Gasoline Association of America Technical Manual (4th ed) (1941) with permission (based on data provided by George Granger Brown).

1. To calculate the **bubble point temperature** (given the total pressure and liquid composition), you can write Equation (19.5a) as $y_i = K_i x_i$. Also, you know that $\sum y_i = 1$ in the vapor phase. Thus for a binary

$$1 = K_1 x_1 + K_2 x_2 \quad (19.6)$$

in which the K_i 's are functions of only the temperature. Because each of the K_i 's increases with temperature, Equation (19.6) has only one positive root. You can employ Newton's method (or Polymath on the CD) to get the root (see Appendix L2) if you can express each K_i as an explicit function of temperature. If not, you have to assume a series of temperatures, look up or calculate K_i , and then calculate each term in Equation (19.6). After you bracket the value of 1, you can interpolate to get T , which satisfies Equation (19.6).

For an ideal solution, Equation (19.6) becomes

$$p_{\text{total}} = p_1^* x_1 + p_2^* x_2 \quad (19.7)$$

$$\sum y_i = \frac{p_1^* x_1(T_{\text{bp}})}{p_{\text{total}}} + \frac{p_2^* x_2(T_{\text{bp}})}{p_{\text{total}}} = 1 \quad (19.7a)$$

Note that this equation is nonlinear and requires an iterative solution to determine T_{bp} .

You might use Antoine's equation for p_i^* to formulate an equation explicit in T . Solve it as described above in connection with Equation (19.6). Once the bubble point temperature is determined, you can calculate the *vapor composition* from

$$y_i = \frac{p_i^* x_i}{p_{\text{total}}}$$

A degree-of-freedom analysis for the bubble point temperature for a binary mixture shows the degrees of freedom are zero:

$$\text{Total variables} = 2 \times 2 + 2: x_1, x_2; y_1, y_2; p_{\text{total}}, T$$

$$\text{Prespecified values of variables} = 2 + 1: x_1, x_2; p_{\text{total}}$$

$$\text{Independent equations} = 2 + 1: y_1 = K_1 x_1, y_2 = K_2 x_2; y_1 + y_2 = 1$$

2. To **calculate the dew point temperature** (given the total pressure and vapor composition), you can write Equation (19.5a) as $x_i = y_i/K_i$ and you know $\sum x_i = 1$ in the liquid phase. Consequently, you want to solve the equation:

$$1 = \frac{y_1}{K_1} + \frac{y_2}{K_2} \quad (19.8)$$

in which the K 's are a function of temperature, as explained for the bubble point temperature calculation. For an ideal binary solution, Equation (19.8) becomes

$$1 = p_{\text{total}} \left[\frac{y_1}{p_1^*(T_{\text{dp}})} + \frac{y_2}{p_2^*(T_{\text{dp}})} \right] \quad (19.8a)$$

Equation (19.8a) is also nonlinear requiring an iterative numerical solution.

To calculate the composition of the liquid phase, you use

$$x_i = \frac{y_i p_{\text{total}}}{p_i^*}$$

The degree-of-freedom analysis is similar to that for the bubble point temperature calculation.

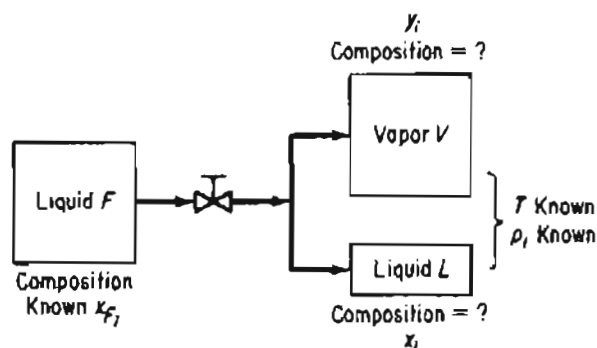


Figure 19.9 Flash vaporization with vapor and liquid in equilibrium.

3. To calculate the amount of the respective vapor and liquid phases that evolve at equilibrium when a liquid of known composition x_{Fi} flashes (**flash vaporization**) at a known temperature and pressure, you use Equation (19.5a) together with a material balance. Figure 19.9 illustrates the open, steady-state process.

For a binary mixture, a mole balance for component i gives

$$F x_{Fi} = L x_i + V y_i \quad (19.9)$$

where F is the moles of liquid to be flashed, L is the moles of liquid at equilibrium, and V is the moles of vapor at equilibrium. Introduction of $y_i = K_i x_i$ into Equation (19.9) gives

$$F x_{Fi} = L \left(\frac{y_i}{K_i} \right) + V y_i$$

so that

$$y_i = \frac{F x_{Fi}}{\frac{L}{K_i} + (F - L)} = \frac{x_{Fi}}{1 - \frac{L}{F} \left(1 - \frac{1}{K_i} \right)} \quad (19.10)$$

where L/F is the liquid fraction resulting from vaporization of the liquid feed. Consequently, for a binary mixture, since $\sum y_i = 1$, you want to solve the following equation

$$1 = \frac{x_{F1}}{1 - \frac{L}{F} \left(1 - \frac{1}{K_1} \right)} + \frac{x_{F2}}{1 - \frac{L}{F} \left(1 - \frac{1}{K_2} \right)} \quad (19.11)$$

for L/F (which must be positive). Numerous computer programs exist to solve the flash vaporization problem.

Based on the above equations, you can prepare figures such as Figures 19.3–19.6 for binary mixtures.

Table 19.1 summarizes the phase equilibrium calculations.

TABLE 19.1 Summary of the Information Involved with Typical Phase Equilibrium Calculations

Type	Known* Information	Variables to be Calculated	Equation to Use
Bubble point temperature	p_{total}, x_i	T, y_i	19.6
Dew point temperature	p_{total}, y_i	T, x_i	19.8
Bubble point pressure	T, x_i	p_{total}, y_i	19.6
Dew point pressure	T, y_i	p_{total}, x_i	19.8
Flash	$p_{\text{total}}, T, x_{F,i}$	$\frac{L}{F}, y_i, x_i$	19.11

* K_i is assumed to be a known function of T and p_{total} .

We should remark that in this chapter we have assumed that any liquids are miscible. If they are completely immiscible, then each would exert an independent vapor pressure $p_i = p_i^* = y_i p_{\text{total}}$, and the total pressure on the system would be $\sum p_i$.

The next two examples illustrate the details of the vapor-liquid equilibrium calculations.

EXAMPLE 19.3 Bubble-Point Calculation

Suppose that a liquid mixture of 4.0 mol % *n*-hexane in *n*-octane is vaporized. What is the composition of the first vapor formed if the total pressure is 1.00 atm?

Solution

Refer back to Figure 19.5 to view the type relation of T versus x at constant p that is involved in this problem. The mixture can be treated as an ideal mixture because the components are quite similar. As an intermediate step, you can calculate the bubble point temperature using Equation (19.7) or (19.7a). Let's use the Antoine equation to relate p^* to T , substitute the result into Equation (19.7), and solve the resulting equation for T . You have to look up the coefficients of the Antoine equation to obtain the vapor pressures of the two components:

$$\ln(p^*) = A - \frac{B}{C + T}$$

where p^* is in mm Hg and T is in K:

	A	B	C
<i>n</i> -hexane (C_6):	15.8366	2697.55	-48.784
<i>n</i> -octane (C_8):	15.9798	3127.60	-63.633

Basis: 1 kg mol of liquid

You want to solve the following equation to get the bubble point temperature using a nonlinear equation solver:

$$760 = \exp\left(15.8366 - \frac{2697.55}{-48.784 + T}\right)0.040 + \exp\left(15.9798 - \frac{3127.60}{-63.633 + T}\right)0.960$$

The solution via polymath is $T = 393.6\text{K}$, for which the vapor pressure of hexane is 3114 mm Hg, and the vapor pressure of octane is 661 mm Hg. The respective mole fractions in the vapor phase are

$$y_{C_6} = \frac{P_{C_6}^*}{p_{\text{total}}} x_{C_6} = \frac{3114}{760}(0.04) = 0.164$$

$$y_{C_8} = 1 - 0.164 = 0.836$$

EXAMPLE 19.4 Flash Calculation for a Binary Liquid Mixture

Calculate the fraction of liquid that will remain at equilibrium when a mixture of 68.6% hexane and 31.4% toluene is vaporized at 80°C and 1 atm.

Solution

You can treat the hexane and toluene mixture as an ideal solution, and use Equation (19.11) in solving the problem.

Steps 3 and 4

Remember that the percentages given in the problem statement are in mass, so that the first step is to convert the concentrations to mole fractions.

Basis: 100 g solution

Component	Grams	Mol. wt.	g mol	Mol fr.
Hexane	68.6	86.17	0.796	0.70
Toluene	31.4	92.13	0.341	0.30
	100.0		1.137	1.00

Vapor pressure data at 80°C are: Hexane Toluene

p^* (mm Hg) 1020 290

The next step is to calculate the values of K_i :

$$K_{\text{hexane}} = \frac{P_{\text{hexane}}^*}{p_{\text{total}}} = \frac{1020}{760} = 1.34; \quad \frac{1}{K_{\text{hexane}}} = 0.745$$

$$K_{\text{toluene}} = \frac{290}{760} = 0.382; \quad \frac{1}{K_{\text{toluene}}} = 2.621$$

Steps 8 and 9

Introduce the above values into Equation (19.11) to get

$$1 = \frac{0.70}{1 - \frac{L}{F}(1 - 0.745)} + \frac{0.30}{1 - \frac{L}{F}(1 - 2.621)}$$

The solution is

$$\frac{L}{F} = 0.745$$

(The equality of L/F and $1/K_{\text{hexane}}$ is purely coincidental.)

EXAMPLE 19.5 Separation of a Virus from a Culture

Particles such as a virus in a solution (culture) can be separated from the culture by partitioning between two phases. A polymer solution immiscible with the culture solution is added and mixed with the culture. After equilibrium is reached, two phases exist. The virus is found in both the culture solution and the polymer solution.

The data for one experiment is as follows:

- The initial volume of the solution containing the culture and the virus was $V_0 = 3.0 \text{ L}$
- The volume of the polymer solution added to the vessel was $V_P = 0.1 \text{ L}$.
- The partition coefficient $K_{P/C}$ for the virus between the two phases is

$$K_{P/C} = \frac{c_P}{c_C} = 100$$

where c_P = concentration of the virus in the polymer phase, particles/L

c_C = concentration of particles in the culture phase, particles/L

After equilibrium is reached, what is the fraction of the initial virus in the culture phase that is recovered in the polymer phase?

Solution

You want to find

$$\frac{c_P V_P}{c_C V_C}$$

The virus particle balance is

$$V_0 c_0 = V_P c_P + V_C c_C$$

Assume $V_0 = V_C = 3.0$ L after equilibrium is reached. Then

$$\frac{3.0 \text{ L}}{\text{L}} \left| \frac{c_0 \text{ virus particles}}{\text{L}} \right| = \frac{0.1 \text{ L}}{\text{L}} \left| \frac{c_P \text{ virus particles}}{\text{L}} \right| + \frac{3.0 \text{ L}}{\text{L}} \left| \frac{c_C \text{ virus particles}}{\text{L}} \right|$$

Divide both sides of the equation by c_0 and introduce the partition coefficient for c_C to get

$$3.0 = \frac{0.1 c_P}{c_0} + \frac{3.0 c_P}{100 c_0}$$

The solution is

$$3.0 = 0.13 \frac{c_P}{c_0} \text{ so that } \frac{c_P}{c_0} = 23.1$$

and

$$\frac{c_P}{c_0} \times \frac{V_P}{V_0} = 0.77.$$

SELF-ASSESSMENT TEST

Questions

1. The heading of a recent article in the *Journal of Chemical Education*, **72**, 204–205 (1995) was:

Raoult's Law is a Deception

What did the author mean by such a provocative title?

2. When should you use Henry's law and when should you use Raoult's law?
3. As you know, the higher the fuel volatility, the higher the emissions from the fuel. Refiners adjust the butane content of gasoline because it is a high octane, relatively cheap hydrocarbon that helps cars to start and warm up easily. Similarly, blending ethanol (more expensive than butane) with gasoline raises the volatility of the blend above that of straight gasoline, which makes the emissions problem worse. If you ignore costs, will adding two mole % ethanol or butane to octane yield a product that has a higher pressure over the liquid solution?
4. Can you make a plot of the partial pressures, and total pressure of a mixture of heptane and octane given solely that the vapor pressure of heptane is 92 mm Hg and that of octane is 31 mm Hg at a given temperature?

5. Why is it necessary to remove much of the water vapor that exists in a natural gas supply before sending the gas through a pipeline?

Problems

1. Calculate the boiling point temperature of 1 kg of a solution of 70% ethylene glycol (antifreeze) in water at 1 atm. Assume the solution is ideal.
2. For a system comprised of a liquid mixture of benzene and toluene at 1 atm, answer the following questions:
 - a. The normal boiling point of benzene is 80.0°C. What is the mole fraction of benzene in the liquid and vapor phases in the cited system?
 - b. The normal boiling point of toluene is 110.4°C. What is the mole fraction of benzene in the liquid and vapor phases for the cited system?
 - c. At 100°C, what is the mole fraction of the benzene in the liquid and vapor phases?
3. When a mixture of 50 mol % benzene and 50 mol % toluene was flashed at equilibrium at 1 atm, 90% of the feed was vaporized. What were the mole fractions of the benzene in the liquid and vapor phases, and what was the temperature of the system?

Thought Problems

1. The fluid in a large tank caught on fire 40 minutes after the start of a blending operation in which one grade of naphtha was being added to another. The fire was soon put out and the naphtha was moved to another tank. The next day blending was resumed in the second tank; 40 minutes later another fire started. Can you explain the reason for this sequence of events? What might be done to prevent such accidents?
2. CO₂ can be used to clean optical or semiconductor surfaces and remove particles or organic contaminants. A bottle of CO₂ at 4000 kPa is attached to a jet that sprays onto the optical surface. Two precautions must be taken with this technique. The surface must be heated to about 30–35°C to minimize moisture condensation, and you must employ a CO₂ source with no residual heavy hydrocarbons (lubricants) to minimize recontamination in critical cleaning applications. Describe the physical conditions of the CO₂ as it hits the optical surface. Is it gas, liquid, or solid? How does the decontamination take place?
3. The advertisement reads “Solid dry ice blocks in 60 seconds right in your own lab! Now you can have dry ice available to you at any time, day or night, with this small, safe, efficient machine and readily available CO₂ cylinders. No batteries or electrical energy are required.” How is it possible to make dry ice in 60 seconds without a compressor?
4. An inventor is trying to sell a machine that transforms water vapor into liquid water without ever condensing the water vapor. You are asked to explain if such a process is technically possible. What is your answer?
5. Examine the statements below:
 - a. “The vapor pressure of gasoline is about 97 kPa at 54°C.”
 - b. “The vapor pressure of the system, water-furfural diacetate, is 101 kPa at 99.96°C.”

Are the statements correct? If not, correct them. Assume the numerical values are correct.

6. To maintain safe loading of hydrocarbon fluids, one of the many objectives of the Coast Guard is to prevent underpressuring of the tank(s) of the vessel being loaded. Overpressuring is easy to understand—to much fluid is pumped into a tank. How can underpressuring occur?

Discussion Problems

1. Gasoline tanks that have leaked have posed a problem in cleaning up the soil at the leak site. To avoid digging up the soil around the tank, which is located 5–10 m deep, it has been suggested that high pressure steam be injected underneath the gasoline site via wells to drive the trapped gasoline into a central extraction well which, under vacuum, would extract the gasoline. How might you design an experiment to test the concept of removal? What kinds of soils might be hard to treat? Why do you think steam was used for injection rather than water?
2. How to meet increasingly severe federal and state regulations for gasoline, oxygenated fuels, and low-sulfur diesel fuel represents a real challenge. The table below shows some typical values for gasoline components prior to the implementation of the regulations in the State of California, and the limits afterwards.

Fuel Parameter	Former (Typical Gasoline)	Current (Limit for Refineries)
Sulfur (ppmw)	150	40
Benzene (vol %)	2	1
Olefins (vol %)	9.9	6
Oxygen (wt %)	0	2.2
Boiling point for 90% of the gasoline (°F)	330	300

Read some of the chemical engineering literature, and prepare a brief report on some of the feasible and economic ways that have been proposed or used to meet the new standards. Will enforcing emission standards on old automobiles (or junking them) be an effective technique of reducing emissions relative to modifying the gasoline? What about control of evaporative emissions from the fuel tank. What about degradation or malfunction of emission controls? Etc.

2. The EPA negotiated an agreement on reformulated gasoline that included a waiver permitting the use of higher vapor pressure gasoline with added ethanol than gasoline without ethanol. Considerable argument occurred because the ethanol-gasoline fuel leads to more volatile organic compounds finding their way into the atmosphere. Supposedly blending 10% ethanol into gasoline increases the vapor pressure of the mixture over ethanol free gasoline by 1 psi measured as Reid vapor pressure—RVP). Tests show that the evaporation of hydrocarbons increases by 50%. What would be the vapor pressure of a 10% ethanol-gasoline mixture versus the vapor pressure of gasoline alone at 25°C, and indicate whether the reported 50% increase in vaporization of hydrocarbons from the fuel

seems reasonable. (Note the aromatics in the gasoline are not more than 25% and the benzene is not more than 1% by volume.) What other factors must be taken into account in blending gasoline?

Looking Back

In this chapter we showed how the phase rule applies to systems in equilibrium. Then we described how to calculate the partial pressure of the components in a vapor-liquid mixture at equilibrium using Henry's law, Raoult's law, and the equilibrium coefficient K_i . Finally, we explained how to determine T , p , x , y , at equilibrium and the fraction of liquid vaporized for ideal and real solutions.

GLOSSARY OF NEW TERMS

Azeotrope Point at which the dew point and the bubble point curves coincide.

Bubble point Temperature at which vapor first forms from a liquid at given pressure.

Dew point Temperature at which a liquid first forms from a vapor at constant pressure.

Distribution coefficient See K-value.

Equilibrium ratio See K-value.

Flash Partial vaporization of a liquid of a given composition at a fixed temperature and pressure.

Gibb's phase rule A relation that gives the degrees of freedom for intensive variables in a system in terms of the number of phases and number of components.

Henry's law A relation between the partial pressure of the gas in the gas phase and the mole fraction of the gas in the liquid phase at equilibrium.

Ideal solution A system whose properties, such as vapor pressure, specific volume, and so on, can be calculated from the knowledge only of the corresponding properties of the pure components and the composition of the solution.

Invariant A system in which no variation of conditions is possible without one phase disappearing.

K-value A parameter (distribution coefficient) used to express the ratio of the mole fraction in one phase to the mole fraction of the same component in another phase.

Phase A part of a system that is *chemically and physically* uniform throughout. This definition does not necessarily imply that the phase is continuous.

Phase equilibrium The phases present in a system are invariant as are the phase properties.

Raoult's Law A relation that relates the partial pressure of one component in the vapor phase to the mole fraction of the same component in the liquid phase.

Vapor-liquid equilibria Graphs showing the concentration of a component in a vapor-liquid system as a function of temperature and/or pressure.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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PROBLEMS

- *19.1 A vessel contains liquid ethanol, ethanol vapor, and N_2 gas at equilibrium. How many phases, components, and degrees of freedom are there according to the phase rule.
- *19.2 What is the number of degrees of freedom according to the phase rule for each of the following systems:
(a) Solid iodine in equilibrium with its vapor
(b) A mixture of liquid water and liquid octane (which is immiscible in water) both in equilibrium with their vapors
- *19.3 A mixture of water, acetic acid, and ethyl alcohol is placed in a sealed container at 40°C at equilibrium. How many degrees of freedom exist according to the phase rule for this system? List a specific variable for each degree of freedom.
- *19.4 (a) A system contains 2 components at equilibrium. What is the maximum number of phases possible with this system? Give your reasons for your answer.
(b) A two-phase system is specified by fixing the temperature, the pressure, and the amount of one component. How many components are there in the system at equilibrium? Explain.
- *19.5 Liquid water in equilibrium with water vapor is a system with how many degrees of freedom?
- *19.6 Liquid water in equilibrium with moist air is a system with how many degrees of freedom?

- *19.7 You have a closed vessel that contains $\text{NH}_4\text{Cl(s)}$, $\text{NH}_3\text{(g)}$, and HCl(g) in equilibrium. How many degrees of freedom exist in the system?
- *19.8 In the decomposition of CaCO_3 in a sealed container from which the air was initially pumped out, you generate CO_2 and CaO . If not all of the CaCO_3 decomposes at equilibrium, how many degrees of freedom exist for the system according to the Gibbs phase rule?
- *19.9 Answer the following questions true or false:
- The critical temperature and pressure are the highest temperature and pressure at which a binary mixture of vapor and liquid can exist at equilibrium.
 - Raoult's law is best used for a solute in dilute solutions.
 - Henry's law is best used for a solute in concentrated solutions.
 - A mixture of liquid butane and pentane can be treated as an ideal solution.
 - The liquid phase region is found above the vapor phase region on $p - x - y$ chart.
 - The liquid phase region is found below the vapor phase region on a $T - x - y$ chart.
- *19.10 Determine if Henry's Law applies to H_2S in H_2O based on the following measurements at 30°C :

Liquid mole fraction $\times 10^2$	Pressure (kPa)
0.0003599	20
0.0004498	30
0.0005397	40
0.0008273	50
0.0008992	60
0.001348	90
0.001528	100
0.003194	200
0.004712	300
0.007858	500
0.01095	700
0.01376	900
0.01507	1000

- *19.11 Determine the equilibrium concentration in mg/L of chloroform in water at 20°C and 1 atm assuming that gas and liquid phases are ideal, and the mole fraction of the chloroform in the gas phase is 0.024. The Henry constant for chloroform is $H = 170$ atm/mol fraction.
- *19.12 Water in an enclosed vessel at 17°C contains a concentration of dissolved oxygen of 6.0 mg/L. At equilibrium, determine the concentration of oxygen in the air space above the water in mg/L. Henry's law constant is 4.02×10^6 kPa/mol fraction and the pressure in the vessel is 1 atm.
- **19.13 You are asked to remove 90% of the sulfur dioxide in a gas stream of air and sulfur dioxide that flows at the rate of 85 cubic meters per minute and contains 3% sulfur

dioxide. The sulfur dioxide is to be removed by a stream of water. The entering water contains no sulfur dioxide. The temperature is 290 K and the pressure on the process is one atmosphere. Find (a) the kilograms of water per minute need to remove the sulfur dioxide assuming that the exit water is in equilibrium with the entering gas, and (b) the ratio of the water stream to the gas stream. The Henry's Law constant for sulfur dioxide at 290 K is 43 atm/mol fraction.

- *19.14** A tank contains a liquid composed of 60 mole percent toluene and 40 mole percent benzene in equilibrium with the vapor phase and air at 1 atm and 60°F.

What is the concentration of hydrocarbons in the vapor phase?

If the lower flammability limit for toluene in air is 1.27% and benzene is 1.4%, is the vapor phase flammable?

- *19.15** Fuel tanks for barbeques contain propane and n-butane. At 120°F, if an essentially full tank of liquid that contains liquid and vapor in equilibrium and exhibits a pressure of 100 psia, what is the overall (vapor plus liquid) mole fraction of butane in the tank.

- *19.16** Based on the following vapor pressure data, construct the temperature-composition diagram at 1 atm for the system benzene-toluene, assuming ideal solution behavior.

Temperature °C	Vapor pressure, mm Hg	
	Benzene	Toluene
80	760	300
92	1078	432
100	1344	559
110.4	1748	760

- *19.17** Sketch a T-x-y diagram that shows an azeotrope and locate and label the bubble and dew lines and the azeotrope point.
- *19.18** What is (a) the pressure in the vapor phase, and (b) the composition of the vapor phase in equilibrium with a liquid mixture of 20% pentane and 80% heptane at 50°F? Assume the mixture is an ideal one at equilibrium.
- *19.19** Methanol has a flash point at 12°C at which temperature its vapor pressure is 62 mm Hg. What is the flash point (temperature) of a mixture of 75% methanol and 25% water. Hint: The water does not burn.
- *19.20** Two kilograms of a mixture of 50-50 benzene and toluene is at 60°C. As the total pressure on the system is reduced, at what pressure will boiling commence? What will be the composition of the first bubble of liquid?
- **19.21** The normal boiling point of propane is -42.1°C and the normal boiling point of n-butane is -0.5°C. (a) Calculate the mole fraction of the propane in a liquid mixture that boils at -31.2°C and 1 atm. (b) Calculate the corresponding mole fraction of the propane in the vapor at -31.2°C. (c) Plot the temperature vs. propane mole fraction for the system of propane and butane.
- *19.22** In the system n-heptane, n-octane at 200°F, determine the partial pressure of each component in the vapor phase at liquid mole fractions of n-heptane of 0, 0.2, 0.4, 0.6, 0.8 and 1.0. Also calculate the total pressure above each solution.

Plot your results on a P-x diagram with mole fractions of C_7 increasing to the right and mole fractions of C_8 increasing to the left. The ordinate should be pressure in psia.

Read from the plotted graph the following information:

The total pressure and the partial pressure of each component at a mole fraction of $C_7 = 0.47$ in the liquid.

- ✓ *19.23 Calculate the bubble point of a liquid mixture of 80 mole% n-hexane and 20 mole% n-pentane at 200 psia.
- ✓ *19.24 Calculate the dew point of a vapor mixture of 80 mole% n-hexane and 20 mole% n-pentane at 100 psia.
- ✓ **19.25 A mixture of 50 mole% benzene and 50 mole% toluene is contained in a cylinder at 39.36 in. Hg absolute. Calculate the temperature range in which a two phase system can exist.
- ✓ **19.26 A liquid mixture of n-pentane and n-hexane containing 40 mol per cent n-pentane is fed continuously to a flash separator operating at 250°F and 80 psia. Determine:
(a) The quantity of vapor and liquid obtained from the separator per mol of feed.
(b) The composition of both the vapor and the liquid leaving the separator.
- ***19.27 One hundred moles per minute of a binary mixture of A and B are separated in a two stage (serial) process. In the first stage, the liquid and vapor flow rates exiting from the stage are each 50 moles per minute. The liquid stream is then passed into a second separator that operates at the same temperature as the first stage, and the respective exit streams of liquid and vapor from the second stage are each 25 moles per minute. The temperature is the same for each stage, and at that temperature, the vapor pressure of A is 10 kPa while the vapor pressure of B is 100 kPa. Treat the liquids and vapors as ideal.
- Calculate the compositions of all of the streams in the process, and calculate the pressure in each stage.
- **19.28 Most combustible reactions occur in the gas phase. For any flammable material to burn both fuel and oxidizer must be present, and a minimum concentration of the flammable gas or vapor in the gas phase must also exist. The minimum concentration at which ignition will occur is called the lower flammable limit (LFL). The liquid temperature at which the vapor concentration reaches the LFL can be found experimentally. It is usually measured using a standard method called a "closed cup flash point" test. The "flash point" of a liquid fuel is thus the liquid temperature at which the concentration of fuel vapor in air is large enough for a flame to flash across the surface of the fuel if an ignition source is present.

The flash point and the LFL concentration are closely related through the vapor pressure of the liquid. Thus, if the flash point is known, the LFL concentration can be estimated, and if the LFL concentration is known, the flash point can be estimated. Estimate the flash point (the temperature) of liquid *n*-decane that contains 5.0 mole percent pentane. The LFL for pentane is 1.8% and that for *n*-decane is 0.8%. Assume the propane-*n*-decane mixture is an ideal liquid. Assume the ambient pressure is 100 kPa. This problem has been adapted from *Safety, Health, and Loss Prevention in*

Chemical Processes, eds. J.R. Welker and C. Springer, American Institute of Chemical Engineers, New York (1990), with permission.

- *19.29** You are asked to determine the maximum pressure at which steam distillation of naphtha can be carried out at 180°F (the maximum allowable temperature). Steam is injected into the liquid naphtha to vaporize it. If (1) the distillation is carried out at 160°F, (2) the liquid naphtha contains 7.8% (by weight) nonvolatile impurities, and (3) if the initial charge to the distillation equipment is 1000 lb of water and 5000 lb of impure naphtha, how much water will be left in the still when the last drop of naphtha is vaporized? *Data:* For naphtha the MW is about 107, and p^* (180°F) = 460 mm Hg, p^* (160°F) = 318 mm Hg.

- **19.30** Late in the evening of 21 August 1986 a large volume of toxic gas was released from beneath and within Lake Nyos in the Northwest Province of Cameroon. An aerosol of water mixed with toxic gases swept down the valleys to the north of Lake Nyos, leaving more than 1,700 dead and dying people in its wake. The lake had a surface area of 1.48 km² and a depth of 200–250 m. It took 4 days to refill the lake, hence it was estimated to have lost about 200,000 tons of water during the gas emission. To the south of the lake and in the small cove immediately to the east of the spillway a wave rose to a height of about 25 m.

The conclusion of investigators studying this incident was that the waters of Lake Nyos were saturated with CO₂ of volcanic origin. Late in the evening of 21 August a pulse of volcanic gas—mainly CO₂ but containing some H₂S—was released above a volcanic vent in the northeast corner of the lake. The stream of bubbles rising to the surface brought up more bottom waters highly charged with CO₂ that gushed out increasing the gas flow and hence the flow of water to the surface much as a warm soda bottle overflows on release of pressure. At the surface, the release of gas transformed the accompanying water into a fine mist and sent a wave of water crashing across the lake. The aerosol of water and CO₂ mixed with a trace of H₂S swept down the valleys to the north of the lake leaving a terrible toll of injury and death in its wake.

If the solution at the bottom of the lake obeyed Henry's law, how much CO₂ was released with the 200,000 metric tons of water, and what would be the volume of the CO₂ at SC in cubic meters? At 25°C the Henry's law constant is 1.7×10^3 atm/mol fr.

- *19.31** Examine the statements below:
- (a) "The vapor pressure of gasoline is about 14 psia at 130°F."
 - (b) "The vapor pressure of the system, water-furfural diacetate, is 760 mm Hg at 99.96°C."

Are the statements correct? If not, correct them. Assume the numerical values are correct.

- **19.32** If the pressure in the head space (gas space) in a bioreactor is 110 kPa and 25°C, and the oxygen concentration in the head space is enriched to 39.7%, what is the mole fraction of the dissolved oxygen in the liquid phase? What is the percent excess oxygen dissolved in the liquid phase compared with the saturation value that could be obtained from air alone dissolved in the liquid?

- *19.33 Three separate waste discharge streams from a plant into a river contain the following respective chemicals in the water

	Concentration (g/100 g water)	K
Glycerol	5.5	1.20×10^{-7}
Methyl ethyl ketone (MEK)	1.1	3.065
Phenol	2.1	0.00485

The K values are from Aspen at 20°C.

Estimate the concentration of the respective compounds in the gas phase above each discharge stream at 20°C. Will volatilization from the discharge stream be significant?

CHAPTER 20

LIQUIDS AND GASES IN EQUILIBRIUM WITH SOLIDS

Your objectives in studying this chapter are to be able to:

1. Predict adsorption of gases and liquids on solids at equilibrium.
2. Determine the values of coefficients in adsorption equilibrium relations from physical measurements.

So far in this book you have read about equilibria involving gas and liquids. Equilibria between fluids and solids are also important—they certainly cannot be ignored.

Looking Ahead

In this chapter we discuss the adsorption of gases and liquids on solids when the system is at *equilibrium*. You will learn what some of the relations are that are used to predict the amounts of absorption, and what kinds of data are collected to get the values of the coefficients in the relations.

Main Concepts

Many important processes involve the adsorption of gases or liquids on solids. Some examples for liquids are:

- Decolorizing, drying, or “degumming” of petroleum fractions.
- Odor, taste, and color removal from municipal water supplies.

- Decolorizing of vegetable and animal oils, and of crude sugar syrups.
- Clarification of beverages and pharmaceutical preparations.
- Purification of process effluents and gases for pollution control.
- Solvent recovery from air such as in removing evaporated dry cleaning solvents.
- Dehydration of gases.
- Odor and toxic gas removal from air or vent gases.
- Separation of rare gases at low temperatures.
- Impurity removal from air prior to low-temperature fractionation.
- Storage of hydrogen.

What goes on in adsorption? **Adsorption** is a physical phenomenon that occurs when gas or liquid molecules are brought into contact with a solid surface, the **adsorbent**. Some of the molecules may condense (the **adsorbate**) on the exterior surface and in the cracks and pores of the solid. If interaction between the solid and condensed molecules is relatively weak, the process is called physical adsorption; if the interaction is strong (similar to a chemical reaction), it is called **chemisorption**, or activated adsorption. We focus on equilibria in physical adsorption in this chapter.

Equilibrium adsorption is analogous to the gas–liquid and liquid–liquid equilibria described in previous chapters. Picture a small section of adsorbent surface. As soon as molecules come near the surface, some condense on the surface. A typical molecule will reside on the adsorbent for some finite time before it acquires sufficient energy to leave. Given sufficient time, an equilibrium state will be reached: the number of molecules leaving the surface will just equal the number arriving.

The number of molecules on the surface at equilibrium is a function of the (1) nature of the solid adsorbent, (2) nature of the molecule being adsorbed (the adsorbate), (3) temperature of the system, and (4) concentration of the adsorbate over the adsorbent surface. Numerous theories have been proposed to relate the amount of fluid adsorbed to the amount of adsorbent. The various theories lead to equations that represent the equilibrium state of the adsorption system. Theoretical models hypothesize various physical conditions such as (1) a solid surface on which there is a monomolecular layer of molecules, (2) a multimolecular layer, or (3) capillary condensation.

Figure 20.1 illustrates typical simple equilibrium adsorption isotherms for the adsorption of water vapor on Type 5A molecular sieves at various temperatures. Note how the amount of gas adsorbed decreases as the temperature increases.

No single relation can represent all of the myriad of types of equilibrium data found in practice, as indicated by the variety of curves for isothermal adsorption called **adsorption isotherms**, shown in Figure 20.2.

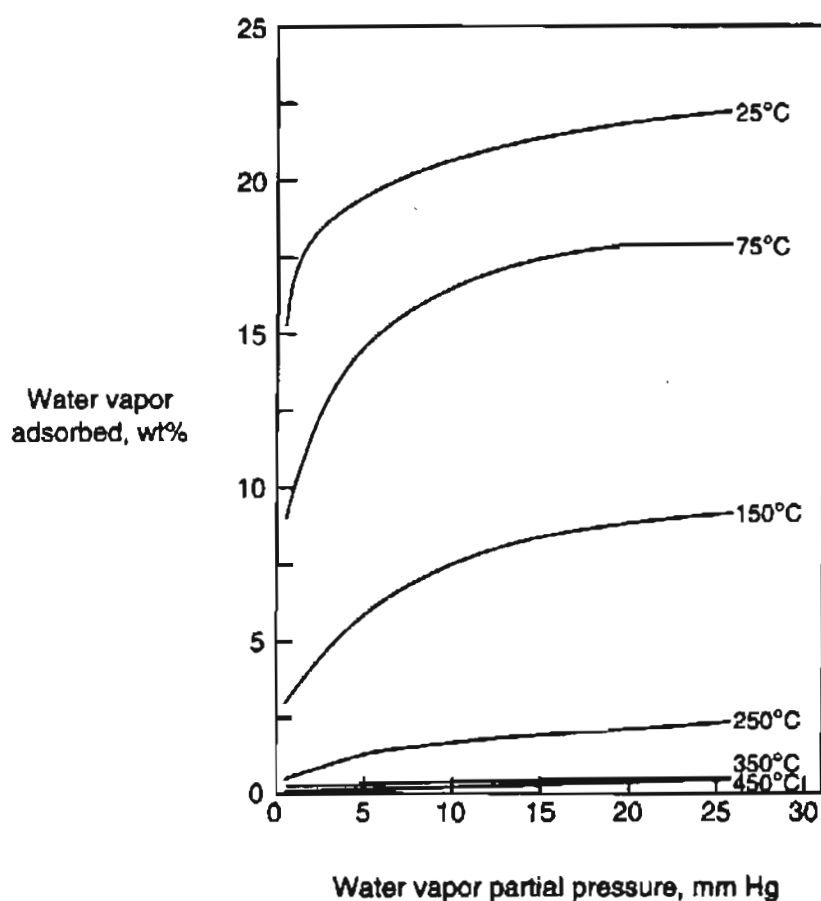


Figure 20.1 Equilibrium adsorption of water on Type 5A molecular sieves.

Two of the simpler equilibrium relations for physical adsorption of Type I in Figure 20.2 relate the amount adsorbed for a single component (the adsorbate) on the adsorbent as a function of the adsorbate partial pressure in the gas phase, or the concentration in the liquid phase, at some temperature. These equations apply for low concentrations at equilibrium.

Freundlich Isotherm

For a gas:

$$y = k_1 p^{n_1}$$

For a liquid:

$$y = k_2 x^{n_2}$$

where p is the partial pressure of the adsorbate in the gas phase

y is the cumulative mass of solute or gas adsorbed (adsorbate) per mass of adsorbent in the solid phase

x is the mass of solute per mass of solution in the liquid phase

and n_i and k_i are coefficients

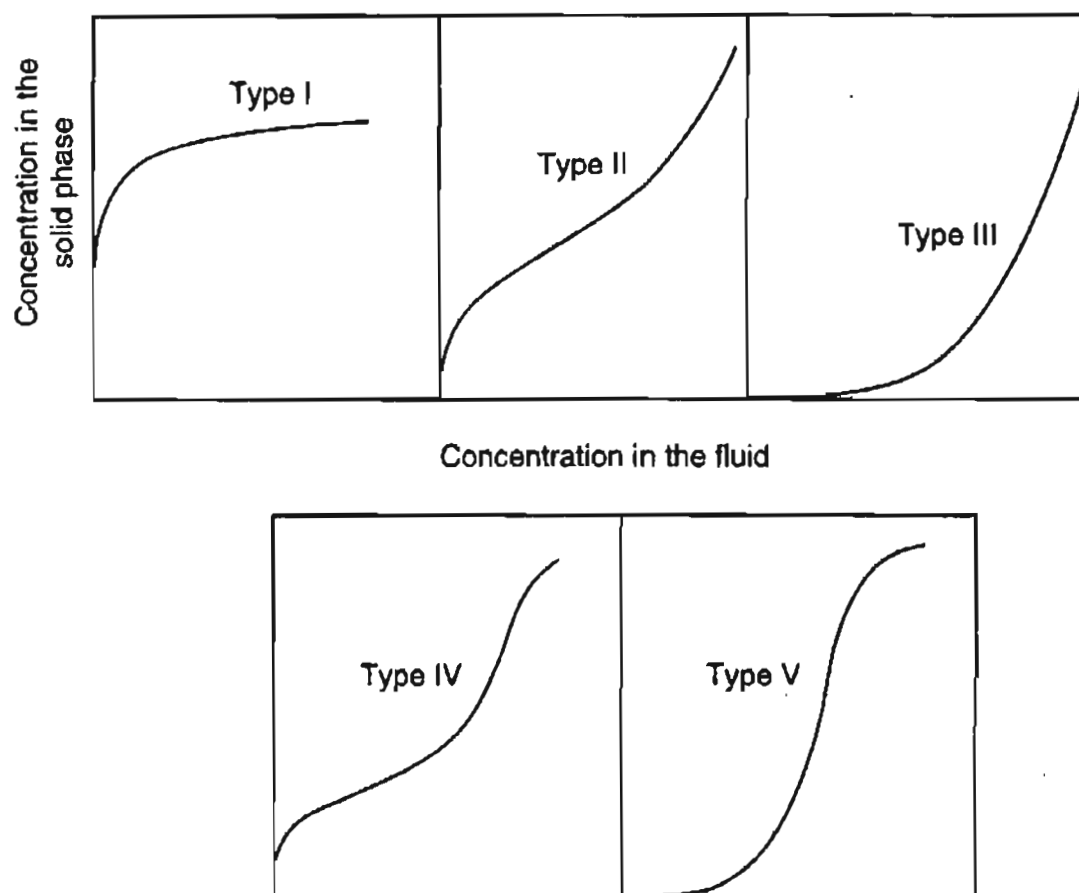


Figure 20.2 Some typical adsorption isotherms. (S. Brunauer, *J. Am. Chem. Soc.*, 62, 1723 (1940).)

Langmuir Isotherm

For a gas:

$$y = \frac{(1 + ak_3)p}{1 + k_3p}$$

For a liquid:

$$y = \frac{(1 + bk_4)x}{1 + k_4x}$$

where a , b , and k_i are coefficient.

The respective equations correspond to mono-layer adsorption. Numerous other relations have been developed to match the particular shapes of the adsorption equilibrium data shown in Figure 20.2. Refer to the references at the end of this chapter.

You can obtain values for the coefficients in the equilibrium isotherms by fitting them to experimental data, as shown in Example 20.1. The expressions $(1+ak_3)$ and $(1+bk_4)$ can be treated as single coefficients in the fitting.

EXAMPLE 20.1 Fitting Adsorption Isotherms to Experimental Data

The following data for the adsorption of CO_2 on 5-A molecular sieves at 298K have been taken from the PhD dissertation *Periodic Countercurrent Operation of Pressure-Swing Adsorption Processes Applied to Gas Separations* by Carol L. Blaney, University of Delaware, 1985, p. 131.

p_{CO_2} (mm Hg)	y (g adsorbed/g sieves)
0	0
25	6.69×10^{-2}
50	9.24×10^{-2}
100	0.108
200	0.114
400	0.127
760	0.137

The estimated coefficients in the respective isotherms obtained by using the regression function in Polymath 5 were:

Freundlich isotherm			Langmuir isotherm		
Model: $y + ap^n$			Model: $ap/(1+bp)$		
$R^2=0.993$			$R^2=0.981$		
Variable	Initial guess	Final value	Variable	Initial guess	Final value
a	1	0.0448	a	100	0.0052
n	0.5	0.1729	b	1	0.0386

The parameter R^2 is a measure of the degree of fit; $R^2 = 1$ is a perfect fit. Figure E20.1 shows the data and the adsorption isotherms.

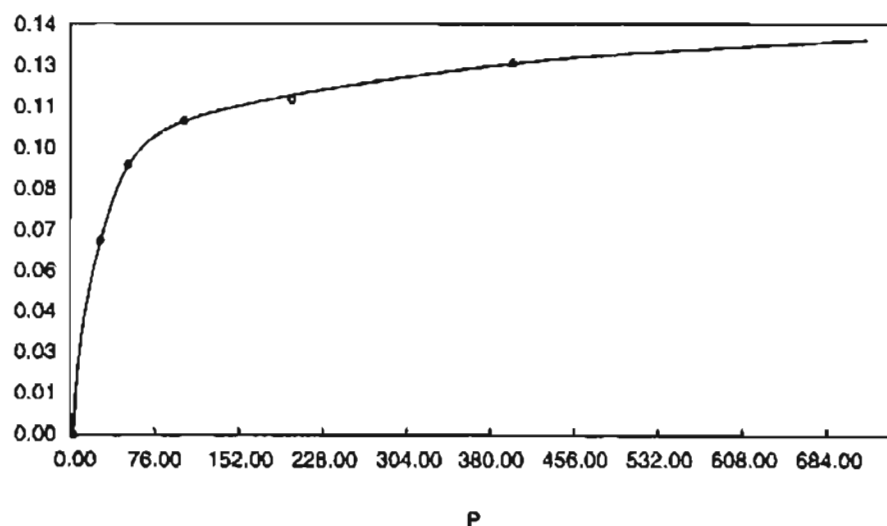


Figure E20.1 The Freundlich and Langmuir isotherms coincide for the adsorption of CO_2 on 5A molecular sieves; O are the experimental points.

A type of constant that is used in environmental studies is the soil sorption partition coefficient, K_{oc} . It characterizes the partitioning of a compound between the solid and liquid phases in soil, and is used to determine the mobility of a compound in soil:

$$K_{oc} = \frac{\frac{\mu\text{g of compound adsorbed}}{\text{g of organic carbon in the soil}}}{\frac{\mu\text{g of compound in the liquid phase}}{\text{mL liquid in the liquid phase}}}$$

How do you use the information about adsorption in practice? One way is to combine it with material balances to help design adsorption equipment. Examine Figure 20.3 in which a carrier G (gas or liquid) is contacted with an adsorbent A (solid). Assume the vessel is well mixed and that the exit streams are in equilibrium with each other.

The mass of G is the mass of the carrier excluding the solute, and the mass of A is also solute free. Often we assume the solution entering is dilute enough so that G is equivalent to the total flow. The material balance corresponding to the process in Figure 20.3 is (note that x and y are *not* mass fractions in what follows)

$$G(x_0 - x_1) = A(y_1 - y_0) \quad (20.1)$$

Usually the A entering is free of solute so that $y_0 = 0$, and thus the material balance becomes

$$G(x_0 - x_1) = Ay_1 \quad (20.2)$$

Example 20.3 below shows how the Freundlich isotherm can be combined with a material balance to solve a design problem.

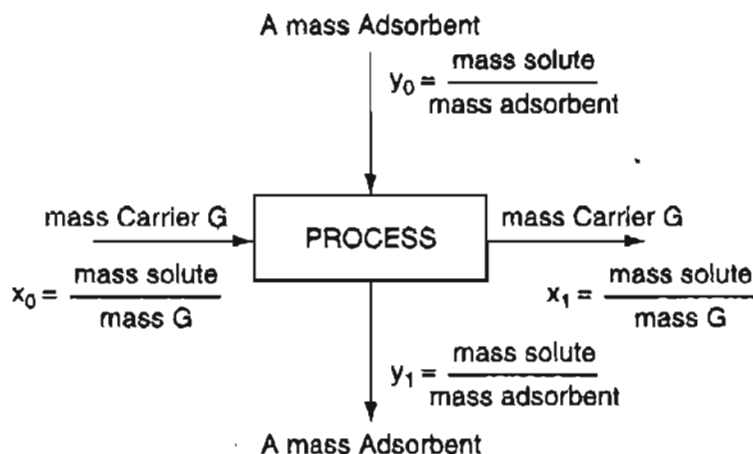


Figure 20.3 The process of adsorption and the notation.

EXAMPLE 20.2 Separation of Biochemicals by Solvent Extraction

Solvent extraction of neutral biochemicals is a common commercial separation method. But for a solute that is highly polar, ion exchange is the preferred method of recovery. In one batch experiment it was found that 1.56 g of soluble streptomycin was adsorbed per g of ion exchange resin from a solution containing 6 g streptomycin/L solution. Because the resin has a high affinity for the adsorption of streptomycin, it is possible to assume that equilibrium is reached in a short period of time after mixing the resin with the solution.

Estimate the grams of resin needed in a batch process to recover as much streptomycin as possible from 1000 L of solution that initially contains 6 g streptomycin/L solution. How many grams of streptomycin would be recovered?

Solution

The simplest procedure is to make a streptomycin balance using the experimental data cited in the problem statement. Assume equilibrium occurs so that the maximum amount of streptomycin is adsorbed.

$$\frac{R \text{ g resin}}{1.56 \text{ g strep. adsorbed}} = \frac{6 \text{ g strep.}}{\text{g resin}} \left| \frac{1000 \text{ L solution}}{\text{L solution}} \right.$$

$$R = 3850 \text{ g}$$

EXAMPLE 20.3 Combination of an Adsorption Isotherm with a Material Balance

You are asked to calculate the minimum mass of activated carbon required to reduce a contaminating solute in a fermentation system from $x_0 = 19.2$ g solute/L solution (for simplicity the value can be treated as g solute/1000 g solution) to $x_1 = 1.4$ g solute/L solution for a 1 L batch of solution by adsorption on activated charcoal in a well-mixed vessel so that the output products are in equilibrium. To solve this problem you collect the following liquid–solid equilibria data. Note that the third column contains calculated, not measured, values.

Measured at equilibrium		
Cumulative g Carbon Added per 1000 g Solution	x g Solute 1000 g Solution	y (Calculated) g Solute Adsorbed g Carbon
0	19.2	—
0.01	17.2	$(19.2 - 17.2)/0.01 = 200$
0.04	12.6	$(19.2 - 12.6)/0.04 = 165$
0.08	8.6	$(19.2 - 8.6)/0.08 = 133$
0.20	3.4	$(19.2 - 3.4)/0.20 = 79$
0.40	1.4	$(19.2 - 1.4)/0.40 = 45$

Solution

Steps 1, 2, 3 and 4

If you fit the data using Polymath, the Freundlich isotherm proves to be

$$y = 37.919 x^{0.583} \quad R^2 = 0.999 \quad (a)$$

and the Langmuir isotherm is

$$y = (29.698 x) / (1 + 0.0955x) \quad R^2 = 0.987 \quad (b)$$

Figure E20.3, the process diagram, shows the flows in and out of the system. From a different viewpoint, the process is equivalent to a batch process in which the materials are put into an empty vessel at the start and removed at the end of the process. Let G be the grams of solution. Because the solution is so dilute, G is essentially equivalent to the grams of solute-free solvent. If you wanted to, you could calculate the ratios of the solute to the solute-free solvent coming in and out of the process, but we will not do so.

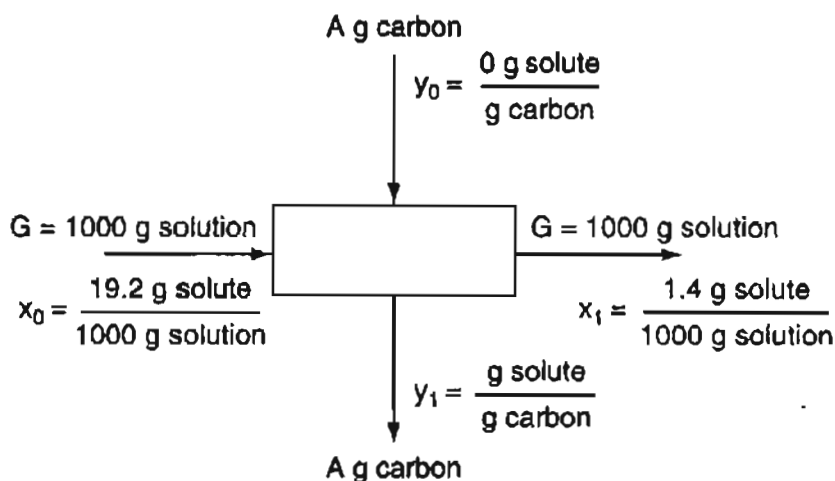


Figure E20.3

Step 5

Let the basis be 1000 g solution (1L).

Steps 6, 7, 8, and 9

Two independent equations are involved in the solution, an equilibrium relation and the material balance. Two unknowns exist, y_1 and the ratio A/G .

Combine Equation (a) with Equation (20.2) to get

$$\frac{A}{G} = \frac{x_0 - x_1}{y_1} = \frac{(19.2 - 1.4) \frac{\text{g solute}}{1000 \text{ g solution}}}{37.919(1.4)^{0.583} \frac{\text{g solute}}{\text{g carbon}}} = \frac{17.8}{46.1} = 0.39 \frac{\text{g carbon}}{1000 \text{ g solution}}$$

Hence, 0.39 g carbon are required.

Step 10

You can check the answer by using the Langmuir isotherm together with the material balance

$$\frac{A}{G} = \frac{19.2 - 1.4}{y_1}$$

$$y_1 = \frac{29.698(1.4)}{1 + 0.0955(1.4)} \quad \text{or } y_1 = 36.67$$

hence

$$\frac{A}{G} = \frac{17.8}{36.67} = 0.48 \text{ g carbon/1000 g solution}$$

Because $y_1 = 46.1$ from the Freudlich isotherm is closer to the experimental value of 45 than is 36.7 from the Langmuir isotherm, the value of 0.39 g as the answer would be preferred. Of course, more carbon will have to be used in practice because to reach equilibrium takes a very long time.

Can you now calculate how much carbon would be required to remove all of the polluting solute?

SELF-ASSESSMENT TEST

Questions

1. Would condensation of water below its dewpoint on charcoal be considered adsorption?
2. Would the conversion of solid NaOH by HCl gas to NaCl be considered adsorption?
3. Would the drying of moist air by charcoal be considered adsorption?
4. Can more than one component be removed simultaneously from a gas or liquid by a solid adsorbent?

Problems

1. One hundred pounds per minute of moist air at 70°F that has a humidity of 0.01 lb H₂O / lb dry air is dehumidified to 0.002 lb H₂O / lb dry air in a dryer. If 7 lb/min of dry silica gel enters the dryer at 70°F, how many lb of H₂O leave the dryer per lb of silica gel entering?
2. The dissertation of Blaney (see Example 20.1) contains the following data for the adsorption of N₂ on activated coconut charcoal at 298K:

P (mm Hg)	y (g mol N_2 /g charcoal) $\times 10^4$
0	0
26.8	0.1562
45.93	0.2945
67.72	0.4149
88.21	0.5354
108.05	0.6360
127.91	0.7406
147.42	0.8477
166.77	0.9458
246.86	1.3786
369.93	1.9808
428.79	2.2396
492.32	2.5430
587.86	2.9713
688.05	3.3996
761.10	3.6851

Determine the coefficients in the Langmuir relation $y = k_0 k_1 p / 1 + k_1 p$.

- Water contains organic color, which is to be extracted with alum and lime. Five parts of alum and lime per million parts of water will reduce the color to 25% of the original color, and 10 parts will reduce the color to 3.5%.

Estimate how much alum and lime as parts per million are required to reduce the color to 0.5% of the original color.

Thought Problems

- Why might a solid adsorbent be used rather than distillation to separate a liquid mixture?
- How might you regenerate an adsorbent used for the separation of (a) gases and (b) liquids?

GLOSSARY OF NEW WORDS

Adsorbent A solid surface on which gas or liquid molecules condense to form a film.

Adsorption The physical process that occurs when gas or liquid molecules are brought into contact with a solid surface and condense on the surface.

Adsorption isotherm The mathematical or experimental relation between the amount a single component adsorbed (the adsorbate) on the adsorbent, and the bulk amount of the adsorbate in a different phase expressed in terms of the partial pressure in the gas phase, or the concentration in the liquid phase, at some temperature.

Chemisorption Adsorption when interaction between the solid and the condensed molecules is relatively strong as contrasted with physical adsorption.

Freundlich isotherm Mathematical relation for adsorption that takes place at equilibrium.

Langmuir isotherm Mathematical relation for adsorption that takes place at equilibrium.

SUPPLEMENTARY REFERENCES

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Web Sites

<http://ias.vub.ac.be/>

<http://www.adsorption.com/publications.htm>

http://www.cheresources.com/l_adsorpt

PROBLEMS

- *20.1 The adsorption of sulfur dioxide by polymer pellets at 0°C is listed below. Using the data below, determine the Langmuir constants, and the Freundlich constants.

p_{SO_2} (mm Hg)	Uptake (mg mol/g)
5	1.75
10	2.20
15	2.40
20	2.62
30	2.75
40	2.85
50	3.00
60	3.05
70	3.12

Do these two isotherms fit the data well?

- *20.2 Emmett studied the adsorption of argon on 0.606 grams of silica gel at -183°C . From the data below, calculate the Freundlich and Langmuir constants.

p (mm Hg)	Uptake (cm^3 at SC)
78.46	55.03
176.92	72.73
224.62	80.00
378.46	106.67
432.31	117.58
515.38	138.18
584.62	166.06

Do these two isotherms fit the data well?

- *20.3 The adsorption of ethane on 5A molecular sieves was studied by Glessner and Myers (1969) at 35°C . Using the data given below, determine:
- If the Langmuir equation can be used to model the data.
 - If the Freundlich equation can be used to model the data.

p (mm Hg)	Uptake (cm^3 at SC/g)
0.17	0.059
0.95	0.318
5.57	1.638
12.09	3.613
111.32	24.236
220.87	34.278
300.05	38.340
401.25	41.779
500.18	44.037
602.74	45.693

- *20.4 In the isothermal adsorption of a mixture of butanol-2 (component 1) and t-amyl alcohol (component 2) on porous activated carbon, the following relation represented the data within an accuracy of $\pm 2\%$

$$c_{s1} = \frac{1.06c_{f1}^{1.217}}{c_{f1}^{0.812} + 0.626c_{f2}^{0.764}}$$

where c_s = concentration of solute in the solid phase, g/cm^3

c_f = concentration of the solute in the fluid phase, g/cm^3

What would the Freundlich equation be for butanol-2 as a pure liquid?

- *20.5 A solution containing a trace amount of chloroform (12 mg/L) is to be reduced to 1 $\mu\text{g}/\text{L}$ of CCl_4 using activated charcoal as the adsorbent. The Freundlich equation that applies to this system is $y = k C^n$ where C is in mg adsorbate/ L solution after processing, and y is the cumulative mg of adsorbate/ g adsorbent. $k = 100$ and $n = 0.30$

at the temperature of the process. How much activated charcoal is required per L of solution?

- **20.6** One hundred pounds per minute of moist air that includes 1 pound of water vapor flows through a dehumidifier. Dry silica is fed to the process, and flows counter current to the air. The water content of the exit air is reduced to 10^{-3} pound of water per pound of dry air. The water in the exit silica gel is in equilibrium with the water in the entering air. What is the required flow rate of the silica gel per minute? The equilibrium relation that applies to this process is $y = 0.0375p^{0.65}$ where y is the g water/g silica gel and p is the partial pressure of the water in the entering air in mm Hg.
- **20.7** The compound 1, 1-dichloroethane (DE) in air at 40°C and with a dew point of 12°C is to be removed with 2 kg per minute of activated carbon. The entering activated carbon contains 50 g DE per kg of DE free activated carbon, and leaves the process with a DE content of 300 g of DE per kg of DE free activated carbon. Calculate the concentration of DE in the exit air assuming that the DE in the exit air is in equilibrium with the exit activated carbon. The barometer is 770 mm Hg. The equilibrium relation for the DE is $y = 0.089p^{0.51}$ where y is the g of DE adsorbed per g of activated charcoal, and p is the partial pressure in the gas phase of the DE in mm Hg. How many g mol of bone dry air pass through the process per minute?
- *20.8** The partition of a compound between soil and water can be estimated by using a soil adsorption coefficient K_{OC}

$$K_{\text{OC}} = \frac{\frac{\text{mass of compound adsorbed in } \mu\text{g}}{\text{mass of organic carbon in the soil in g}}}{\frac{\text{mass of compound in the liquid in } \mu\text{g}}{\text{volume of the liquid in mL}}}$$

Values of K_{OC} for low adsorption are in the range $2.5 > \log_{10}(K_{\text{OC}}) > 1.5$.

How much nitrobenzene will be adsorbed at equilibrium from 1 L of a saturated solution in water at 20°C by 1 kg of soil that has a carbon content of 11%? Data: The solubility of nitrobenzene in water is 0.19 g/100 g water at 20°C , and $\log_{10}(K_{\text{OC}}) = 2.27$.

PART 4

ENERGY BALANCES

CHAPTER	PAGE
21 Energy: Terminology, Concepts, and Units	607
22 Introduction to Energy Balances for Processes without Reaction	645
23 Calculation of Enthalpy Changes	681
24 Applications of Energy Balances in the Absence of Chemical Reactions	717
25 Energy Balances: How to Account for Chemical Reactions	763
26 Energy Balances that Include the Effects of Chemical Reaction	802
27 Ideal Processes, Efficiency, and the Mechanical Energy Balance	836
28 Heats of Solution and Mixing	864
29 Humidity (Psychrometric) Charts and Their Use	884

We now take up the second prominent topic in this book, energy balances. To provide publicly acceptable, effective, and yet economical conversion of our resources into energy and to properly utilize the energy so generated, you must understand the basic principles underlying the generation, uses, and transformation of energy in its different forms. How often have you seen the headline

Energy Crunch Worsens

or its analog? No question exists as to the increase in the long-run use of energy. Figure Part 4.1 shows the forecast of world energy demand to the year 2020. Figure Part 4.2 shows where the energy goes.

The answer to questions such as

- How can energy costs be reduced?
- How can "clean" energy be provided economically?
- Is thermal pollution inherently necessary?
- What is the most economic source of fuel?
- What can be done with waste heat?
- How much steam at what temperature and pressure are needed to heat a process?

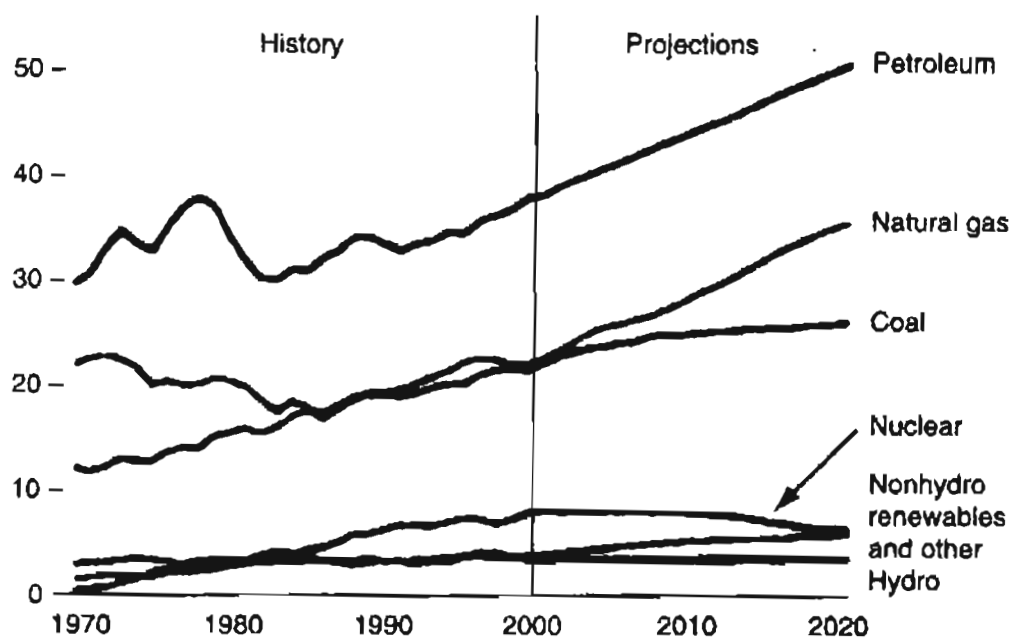
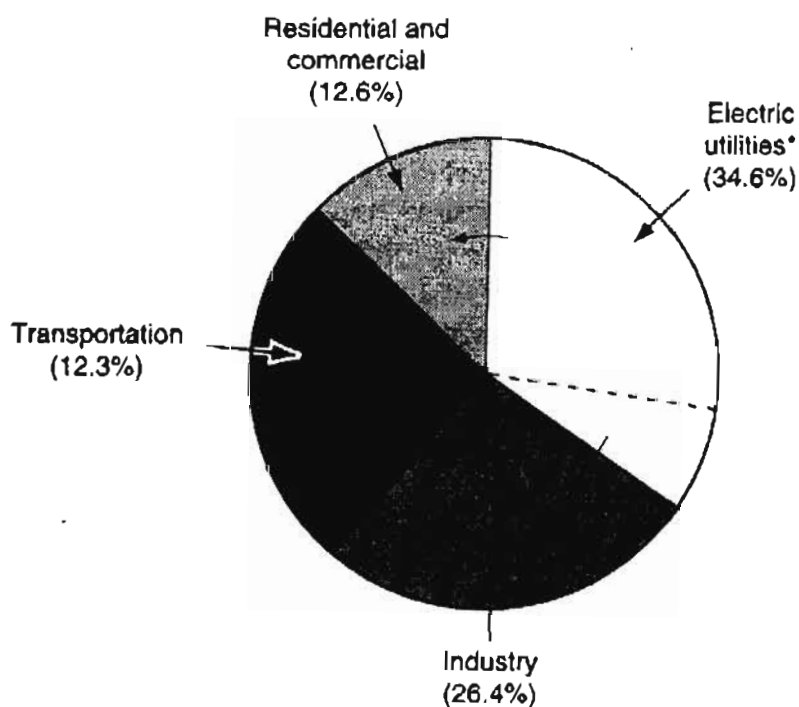


Figure Part 4.1 Past and predicted energy consumption by categories (in quadrillion Btu). (Source: Energy Information Administration, *Annual Energy Review 1999*, DOE/EIA-0384(99) (Washington, DC, July 2000). **Projections:** Tables A1 and A18.)



*Dashed line shows that one-third of the electric power is used by industry and two-thirds by the residential and commercial sector.

Figure Part 4.2 Energy Usage by Category

and related questions can only arise from an understanding of the treatment of energy transfer by natural processes or machines. As an example of a problem you might face, look at the following list of recommended changes made by an evaluation of an operating plant:

Recommendation	Fuel Conserved*	Energy Savings (Btu $\times 10^6$)	Annual Savings (\$)	Payback (years)
1. Insulate steam lines	NG	386	1040	1.3
2. Install personnel access door	NG	173	460	1.5
3. Replace compressor with gas unit and utilize heat recovery	E	505	8730	1.2
	NG	334	890	
4. Install air curtains	E	125	2160	0.36
	NG	153	410	
5. Install packaged cogeneration	none	none	144,000	3.4
6. Install water treatment station (to clean up discharge)	none	none	21,700	10.6

*NG = natural gas, E = electricity *IEEE Spectrum*, 79 (January, 2001).

What should you choose? What can be done economically to reduce the loss of energy rejected as heat to the surroundings? Can you offer reasonable suggestions at this stage in your professional life?

In Part 4 we discuss energy balances together with the accessory background information needed to understand and apply them correctly. Our main attention will be devoted to heat, work, enthalpy, internal energy, and energy balances associated with chemical reaction.

SUPPLEMENTARY REFERENCES

Web Sites

www.geocities.com/combusem/ENERGY/ world energy and CO₂ projections

www.doe.gov

www.eia.doe.gov/emeu/mecs/iab/chemicals

www.eia.doe.gov/siaf/aeo/results

CHAPTER 21

ENERGY: TERMINOLOGY, CONCEPTS, AND UNITS

21.1 The Terminology Associated with Energy Balances

608

21.2 Types of Energy

613

Your objectives in studying this chapter are to be able to:

1. Define or explain the following terms: energy, system, closed system, nonflow system, open system, flow system, surroundings, property, extensive property, intensive property, state, heat, work, kinetic energy, potential energy, internal energy, enthalpy, initial state, final state, state variable, cyclical process, and path function.
2. Select a system suitable for solving a problem, either closed or open, steady or unsteady state, and fix the system boundary.
3. Distinguish among potential, kinetic, and internal energy.
4. Convert energy in one set of units to another set.
5. Calculate the kinetic and potential energy, the work, and the heat transfer in both SI and AE units for a very simple process.
6. Explain the relation between the two heat capacities in terms of the enthalpy or internal energy, as appropriate.

Some of the difficulty in analyzing processes from the viewpoint of energy balances occurs because of the failure of our language to communicate an exact meaning. Many of the difficulties will disappear if you take care to learn the meaning of the terms we review in this chapter.

Looking Ahead

Before starting an excursion into the semantics associated with energy balances, let us lay out a map of the ground to be covered. We first review a number of terms discussed in previous chapters, particularly Chapter 7, namely

607

system	state
surroundings	steady state
boundary	unsteady state (transient)
open system (flow system)	equilibrium
closed system (nonflow system)	phase
property	intensive property
	extensive property

Next we introduce some new terms with which you may or may not be familiar

isothermal system	independent property
isobaric system	state function
isochoric system	path function
adiabatic system	

Finally, we discuss the types of energy that will be included in the energy balances that will be used in the rest of this book.

21.1 The Terminology Associated with Energy Balances

*When I use a word, it means just what
I choose it to mean, neither more nor less.*

—Humpty Dumpty, as reported by Lewis Carroll

Imagine, for a moment, what engineering would be like if Mr. Dumpty's approach were the norm for communication—in effect, there would be none. Agreement on the meaning of words is as essential as agreement on a system of measurements. You have to be precise when using an energy balance to solve a problem, hence we first review certain terms that have been explained in earlier chapters that occur repeatedly in Part 4 of this book. Table 21.1 summarizes these terms.

You also should become familiar with several new terms, which are listed in Table 21.2.

The terms **adiabatic**, **isothermal**, **isobaric**, and **isochoric**, listed in Table 21.2, are useful to specify conditions that do not change in a process. Be aware that the concept of a **state (or point) function** or **variable** is an important concept to understand. Temperature, pressure, and all of the other intensive variables are known as state variables because between two states their change in value is the same no matter what the path taken between the two states. If two systems are in the same state, their state variables such as temperature or internal energy must be identical. If the state of a system is changed, say by heating so that energy flows in, the values of its state variables

TABLE 21.1 Terminology Pertaining to Energy Balances


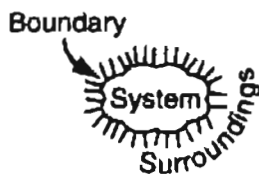
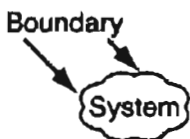


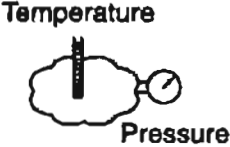
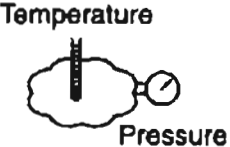








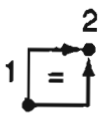
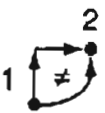
Term	Definition or Explanation		Page
System	The quantity of matter or region of space chosen for study enclosed by a boundary.		137
Surroundings	Everything outside the system boundary.		137
Boundary	The surface that separates the system from the surroundings. It may be a real or imaginary surface, either ridged or movable.		137 136
Open system (flow system)	A system that is open to interchange of mass with the surroundings. Heat and work can also be exchanged.		
Closed system (nonflow system)	A system that does not interchange mass with the surroundings. But heat and work can be exchanged.		136
Property	Observable (or calculable) characteristic of the system such as pressure, temperature, volume, etc.		396
State	Conditions of the system (specified by the values of temperature, pressure, composition, etc.)		396
Steady state	The accumulation in the system is zero, the flows in and out are constant, and the properties of the system are invariant.		138
Unsteady state (transient)	The system is not in the steady state		138
Equilibrium (state)	The properties of the system are invariant; implies a state of balance. Types are thermal, mechanical, phase, and chemical equilibrium.		478
Phase	A part (or whole) of the system that is physically distinct, and macroscopically homogeneous of fixed or variable composition, such as gas, liquid, or solid.		398

TABLE 21.2 ADDITIONAL TERMINOLOGY PERTAINING TO ENERGY BALANCES

Term	Definition or explanation		Page
Adiabatic system	A system that does not exchange heat with the surroundings during a process (perfectly insulated).		619
Isothermal system	A system in which the temperature is invariant during a process.		615
Isobaric system	A system in which the pressure is constant during a process.		615
Isochoric system	A system in which the volume is invariant during a process.		608
State variable (point function) (state function)	Any variable (function) whose value depends only on the state of the system and not upon its previous history (e.g., internal energy).		608
Path variable (function)	Any variable (function) whose value depends on how the process takes place, and can differ for different histories (e.g., heat and work).		611

change, and if the system is returned to its original state, say by cooling so that energy flows out, the values of its state variables return to their original values.

Look at Figure 21.1, which illustrates two processes, A and B, that start at State 1 and terminate at State 2. The change in the value of a state variable is the same by both processes.

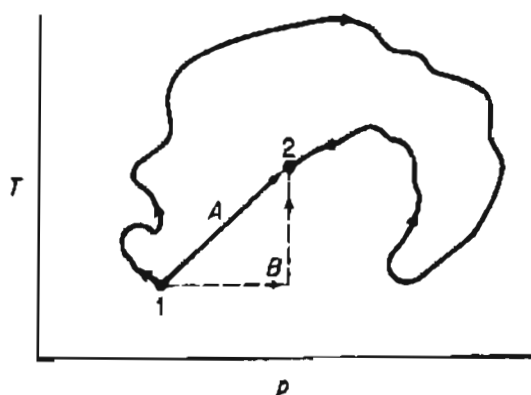


Figure 21.1 Values for the change in state variables are the same for Path A as for Path B, or any other route between States 1 and 2.

A process that proceeds first at constant pressure and then at constant temperature from state 1 to state 2 will yield exactly the same final value for a state variable as one that takes place first at constant temperature and then at constant pressure as long as the end point is the same. The concept of the state or point function is the same as that of an airplane passenger who plans to go straight to New York from Chicago but is detoured by way of Cincinnati because of bad weather. When he arrives in New York, he is the same distance (the state variable) from Chicago whichever way he flies, hence the value of the state variable depends only on the initial and final states. However, the fuel consumption of the plane may vary considerably, and, in analogous fashion, heat or work, the two **path functions** with which we will work, may vary depending on the specific path chosen. If the passenger were to return to Chicago from New York, the distance from Chicago would be zero at the end of the return trip. Thus, the change in the state variable is zero for a cyclical process, which goes from state 1 to 2 and back to state 1 again.

Let us now mention the units associated with energy. As you know, in the SI system the unit of energy is the joule (J). In the AE system we use Btu, (ft)(lb_f), and (kW)(hr) among others. You can find conversion factors among the energy units listed on the inside of the front cover of this book. What about the calorie? Is the unit archaic? It seems not. Most people are concerned about calories, not Btu or joules. A food package gives you information about calories (see Figure 21.2).

Dr. Lawrence Lamb gave a succinct answer to a letter to the newspaper asking if 500 calories of energy is the same as 500 kcal. He said

Nutrition Facts

Serving Size 2 cookies (26 g)
Servings Per Container 8

Amount Per Serving		Vitamin A 0%	•	Vitamin C 0%	
Calories 110	Calories from Fat 35	Calcium 0%	•	Iron 2%	
% Daily Value*		*Percent Daily Values are based on 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs:			
Total Fat 4g	6%	Total Fat	Calories:	2,000	2,500
Saturated Fat 3g	15%	Sat Fat	Less than	65g	80g
Cholesterol 0mg	0%	Sat Fat	Less than	20g	25g
Sodium 50mg	2%	Cholesterol	Less than	300mg	300mg
Total Carbohydrate 18g	6%	Sodium	Less than	2400mg	2400mg
Dietary Fiber 0g	0%	Total Carbohydrate		300g	375g
Sugars 12g		Dietary Fiber		25g	30g
Protein 1g					

Figure 21.2 Information about the nutrition characteristics of a cookie.

Dear Reader: I usually say calories for people like you, but I do cringe each time because it is not correct.

A calorie is only enough energy to raise the temperature of one mL of water one degree centigrade.

But the word calorie for your food is misused. What you think are calories are actually kilocalories (kcal). One kilocalorie (kcal) equals 1,000 real (sic thermochemical) calories, or is the amount of energy required to raise the temperature of one liter of water one degree centigrade. You are supposed to write kcal with a capital C, and use Calories instead of kilocalories.

Thus, if your diet consists of 2,000 Calories per day, you can calculate the number of joules involved per hour:

$$\frac{2000 \text{ kcal}}{\text{day}} \left| \frac{1000 \text{ cal}}{\text{kcal}} \right| \left| \frac{4.184 \text{ J}}{\text{cal}} \right| \left| \frac{1 \text{ day}}{24 \text{ hr}} \right| = 350,000 \text{ J/hr}$$

Your body converts the food you eat into this amount of heat or work every hour.

SELF-ASSESSMENT TEST

Questions

1. What is the essential difference between the system and the surroundings? Between an open and a closed system? Between a property and a phase?
2. Can a variable be both an intensive and an extensive variable at the same time?
3. Describe the difference between a state variable and a path variable.

Problems

1. What is the value of the change in the specific volume of a gas in a closed container that is first compressed to 100 atm, then heated to increase the temperature by 20%, and finally returned to its original state?
2. If you eat food containing 1800 Calories per day according to an advertisement, you will lose weight. A handbook says that a person uses 20,000 kJ per day given normal waking and sleeping activities. Will the person lose weight if he or she eats food as suggested by the advertisement?

Thought Problems

1. A proposed goal to reduce air pollution from automobiles is to introduce into U.S. domestic gasoline a specified fraction of oxygenated compounds from renewable resources, one of which is ethanol grown from corn. What is your estimate of the fraction of the avail-

able U.S. cropland that would be required to replace 10% of the gasoline with alcohol in all of the annual gasoline production of about 1.2×10^{10} gal/yr? Assume 90.0 bu/acre of corn and 2.6 gal ethanol/bu.

2. Another proposal is to supply 10% of the U.S. oil usage by coal liquefaction. What is your estimate of the percentage of the coal now mined in the United States that would have to be processed in order to fulfill this proposal? Assume 3.26 bbl of liquid per ton of coal.
3. My father is moving to a farm nearby, and wants to build a home. He also wants to buy a windmill to generate his electricity. Will a windmill be ok, or does he have to connect to the electric company (which requires him to install a long electric line at his expense)?

Discussion Problems

1. Consider the following sources of energy that can be used to generate electric power:

Biomass (direct combustion)	Oil shale
Coal	Peat
Ethanol from biomass	Solar thermal
Geothermal	Solar voltaic
Hydropower	Tar sands
Methane from biomass	Vegetable oils
Natural gas	Waves
Ocean thermal	Wind
Oil	

Use reference books and the Internet to estimate the cost in \$/kWh of each source. Briefly discuss the potential for future usage.

2. Can a healthy horse produce power at a rate much greater than one horsepower?

21.2 Types of Energy

Before we begin the discussion of the types of energy we will be including in the energy balance, we need to mention certain notation that will be used. All of the terms in the energy balance will be integrated quantities just as were the terms in the mass balance in Chapter 7. Thus, for example, heat, Q , will be the *net amount of heat transferred to or from the system over a fixed interval no matter how the local transfer occurred at any selected instant of time*. If we have to identify a *rate of transfer*, we will place an overlay dot on the symbol for the variable, thus

\dot{Q} heat transfer per unit time.

Because many of the variables with which we will be working are extensive variables, if we want to designate the related intensive variables, we place an overlay caret (^) on the symbol for the variable, thus

\hat{Q} heat transfer/unit mass

They have invented a term "energy" and the term has been enormously fruitful because it also creates a law by eliminating exceptions because it gives names to things which differ in matter but are similar in form.

—H. Poincare

With these preliminaries out of the way, we next discuss the six types of energy that we will include in our energy balances. The categories have been selected because they help you in problem solving, and allow you to easily tie the results of calculations to the performance of equipment such as turbines, compressors, heat engines, and so on. **Energy** itself is often defined as the capacity to do work or transfer heat, a fuzzy concept. It is easier to understand specific types of energy. Two things energy is *not* is (a) some sort of invisible fluid or (b) something that can be measured directly.

The first two types of energy we discuss, namely work and heat, are **energy transfer** between the system and surroundings without any accompanying mass transfer. These two types of energy *cannot be stored* in a system—they are solely transfers into and out of a system.

21.2-1 Work

Work (W) is a term that has wide usage in everyday life (such as "I am going to work"), but has a specialized meaning in connection with energy balances. Work is a form of energy that represents a **transfer** of energy between the system and surroundings. Work cannot be stored. *Work is positive when the surroundings perform work on the system. Work is negative when the system performs work on the surroundings.*

- **Mechanical work**—work that occurs because of a mechanical force that **moves the boundary** of a system. You might calculate W on the system or by the system as

$$W = \int_{\text{state 1}}^{\text{state 2}} \mathbf{F} \cdot d\mathbf{s} \quad (21.1)$$

where \mathbf{F} is an external force (a vector) in the direction of \mathbf{s} (a vector) acting on the system boundary (or a system force acting at the boundary on the surroundings). However, the amount of mechanical work done by or on a system can be difficult to calculate because (a) the displacement $d\mathbf{s}$ may not be easy to define,

and (b) the integration of $F \cdot ds$ as shown in Equation (21.1) does not necessarily give the amount of work actually being done on the system or by the system. Some of the energy involved may be dissipated as heat. In this text, the symbol W refers to the net work done over a period of time, *not* the rate of work. The latter is the **power**, namely work per unit time.

- **Electrical work**—electrical work occurs when an electrical current passes through an electrical resistance in the circuit. If the system generates an electrical current (e.g., an electrical generator inside the system) and the current passes through an electrical resistance outside the system, the electrical work is negative because the electrical work is done on the surroundings. If the electrical work is done inside the system and the electrical current is generated outside the system, the electrical work is positive.
- **Shaft work**—shaft work occurs by a force acting on a shaft to turn it against a mechanical resistance. When a pump outside the system is used to circulate a fluid in the system, the shaft work is positive. When a fluid in the system is used to turn a shaft that performs work on the surroundings, the shaft work is negative.
- **Flow work**—flow work is performed on the system when fluid is pushed into the system by the surroundings. For example, when a fluid enters a pipe some work is done on the system to force the fluid into the pipe. Similarly, when fluid exits the pipe, the system does some work on the surroundings to push the exiting fluid into the surroundings. Flow work will be described in more detail in Chapter 22.

Note that unless the process (path) under which work is carried out is specified from the initial to the final state of the system, you cannot calculate the value of the work done by integrating Equation (21.1). In other words, work done in going between the initial and final states can have *any* value, depending on the path taken. **Work is therefore called a path function**, and the value of W depends on the initial state, the path, and the final state of the system as illustrated in Example 21.1.

The symbol W represents the *net amount of work done on or by the system over a time interval* no matter how the instantaneous rate of work (the power) occurs.

Suppose a gas in a fixed volume container is heated so that its temperature is doubled. How much work was done on or by the gas during the process? Such a question is easy to answer—no work was done because the boundary of the system (the gas) remained fixed. Let's next look at a case in which the boundary changes.

EXAMPLE 21.1 Calculation of Mechanical Work by a Gas on a Piston Showing How the Path Affects the Value of the Work

Suppose that an ideal gas at 300 K and 200 kPa is enclosed in a cylinder by a frictionless piston, and the gas slowly forces the piston so that the volume of gas expands from 0.1 to 0.2 m³. Examine Figure E21.1a. Calculate the work done by the gas on the piston (the only part of the system boundary that moves) if two different paths are used to go from the initial state to the final state:

Path A: the expansion occurs at constant pressure (**isobaric**) ($p = 200$ kPa)

Path B: the expansion occurs at constant temperature (**isothermal**) ($T = 300$ K)

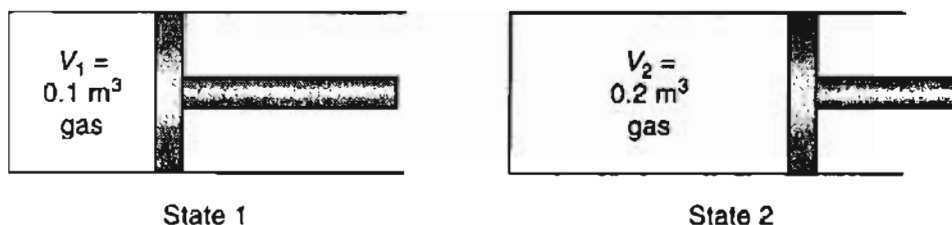


Figure E21.1a

Solution

As explained in more detail in Chapter 27, the piston must be frictionless and the process ideal (occur very slowly) for the following calculations to be valid. Otherwise, some of the calculated work will be changed into a different form of unmeasured energy such as internal energy or heat (which are discussed later). The system is the gas. You are asked to use Equation (21.1) to calculate the work, but because you do not know the force exerted by the gas on the piston, you will have to use the pressure (force/area) as the driving force, which is OK since you do not know the area of the piston anyway, and because p is exerted normally on the piston face. All of the data you need is provided in the problem statement. Let the basis be the amount of gas cited in the problem statement

$$n = \frac{200 \text{ kPa}}{300 \text{ K}} \left| \frac{0.1 \text{ m}^3}{8.314 (\text{kPa})(\text{m}^3)} \right| \frac{(\text{kg mol})(\text{K})}{1} = 0.00802 \text{ kg mol}$$

Figure E21.1b illustrates the two processes.

The mechanical work done by the system on the piston (in moving the system boundary) *per unit area* is

$$W = - \int_{\text{state 1}}^{\text{state 2}} \frac{F}{A} \cdot A ds = - \int_{V_1}^{V_2} p dV$$

Note that by definition, the work done by the system is *negative*. If in the integral alone dV is positive (such as in expansion), the value of the integral will be positive

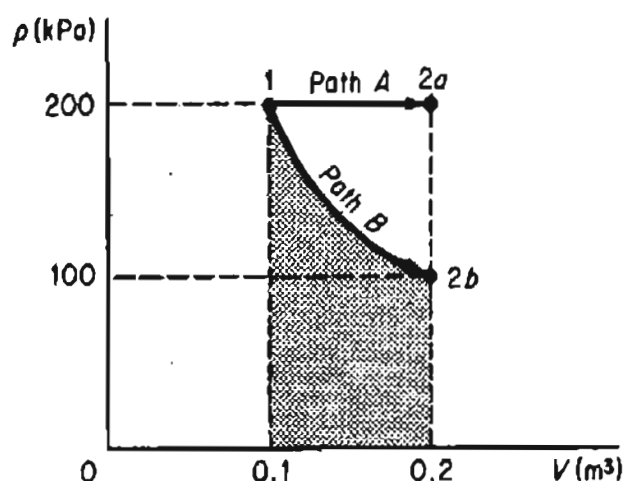


Figure E21.1b

and W negative (work done on the surroundings). If dV is negative, W will be positive (work done on the system).

Path A (the constant pressure process)

$$\begin{aligned} W &= -p \int_{V_1}^{V_2} dV = -p(V_2 - V_1) \\ &= -\frac{200 \times 10^3 \text{ Pa}}{1 \text{ (m}^2\text{)(Pa)}} \left| \frac{1 \text{ N}}{1 \text{ (N)(m)}} \right| \frac{0.1 \text{ m}^3}{1 \text{ (N)(m)}} = -20 \text{ kJ} \end{aligned}$$

Path B (the constant temperature process)

The gas is ideal. Then

$$\begin{aligned} W &= - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \left(\frac{V_2}{V_1} \right) \\ W &= -\frac{0.00802 \text{ kg mol}}{(\text{kg mol})(\text{K})} \left| \frac{8.314 \text{ kJ}}{(\text{kg mol})(\text{K})} \right| \frac{300 \text{ K}}{1} \ln 2 = -20 \ln 2 = -13.86 \text{ kJ} \end{aligned}$$

In Figure E21.1b the two integrals are areas under the respective curves in the p - V plot.

SELF-ASSESSMENT TEST

Questions

1. If the energy crossing the boundary of a closed system is not heat, it must be work. True or false?
2. A pot of water was heated in the stove for 10 minutes. If the water was selected to be the system, did the system do any work during the 10 minutes?

3. Two power stations, A and B, generate electrical energy. A operates at 800 MW for 1 hour and B operates at 500 MW for 2 hours. Which is the correct statement:
- A generated more power than B.
 - A generated less power than B.
 - A and B each generated the same amount of power.
 - Not enough information is provided to reach a decision.

Problems

- A gas cylinder contains N_2 at 200 kPa and 80°C . As a result of cooling at night the pressure in the cylinder drops to 190 kPa and the temperature to 30°C . How much work was done on the gas?
- Nitrogen gas in a cylinder goes through four ideal process stages, as detailed in Figure SAT 21.2 P2. Calculate the work done in Btu by the gas for each stage. The stage from 1 to 2 is isothermal.

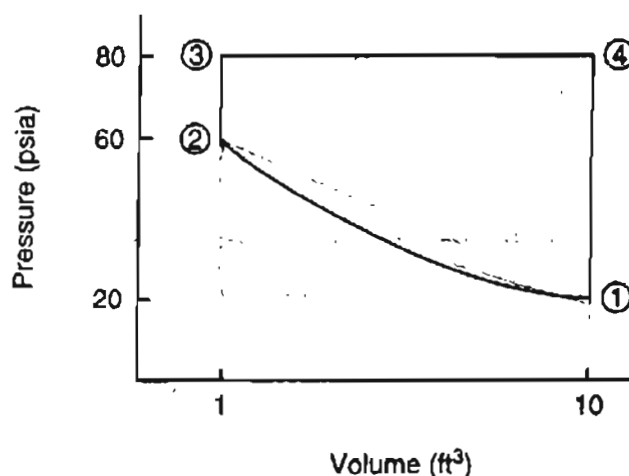


Figure SAT21.2 P2.

Thought Problems

- In AE units power can be expressed in horsepower. Can one horse provide one horsepower for a 10 hour day?
- How can you measure the power of an automobile engine as you drive along at a constant speed?

Discussion Problems

- You can find suggestions in the popular magazines that electric vehicles be covered with solar cells to reduce use of coal-generated electricity. The solar insolation outside the earth's atmosphere is 1 kilowatt per square meter (or square yard, for all practical purposes), yielding 24 kWh per day. Experience has shown that an electric vehicle converted

from a conventional car usually requires a minimum of about 30 kWh stored in the battery. If the surfaces of a car referred to are covered with a layer of solar cells 5 ft by 10 ft, or 50 ft²—about 5 m²—120 kWh/day will be available from the photovoltaic cells.

Carry out an evaluation of this calculation. What deficiencies does it have? Think of the entire transition from solar energy to chemical change in the battery.

2. The Alabama Electric Cooperative dedicated the nation's first compressed air energy storage (CAES) power plant. The \$65 million plant stores compressed air in a cavern during periods when electricity is least expensive and usage is low. During periods of peak demand, the compressed air is heated and expanded in a combustion turbine to generate electricity. One full charge from the 110-MW 24-hour CAES plant can supply the power demand of 11,000 homes.

How satisfactory in the long run will such a plant be?

21.2-2. Heat

*Heat can't flow from a cooler to a hotter, you can try if
you like but you'd far better notter.*

Michael Flanders and Donald Swann,
"At the Drop of Another Hat," Angel Records

In a discussion of *heat* we enter an area in which our everyday use of the term may cause confusion, since we are going to use heat in a very restricted sense when we apply the laws governing energy changes. **Heat (Q)** is commonly defined as that part of the total energy flow across a system boundary that is caused by a temperature difference (potential) between the system and the surroundings (or between two systems). See Figure 21.3. Engineers say "heat" when meaning "heat transfer" or "heat flow." Heat is neither stored nor created. **Heat is positive when transferred to the system.**

A process in which no heat transfer occurs is an **adiabatic process** ($Q = 0$). Examples of an adiabatic process include processes in which the system and its surroundings are at the same temperature and processes in which the system is perfectly insulated.

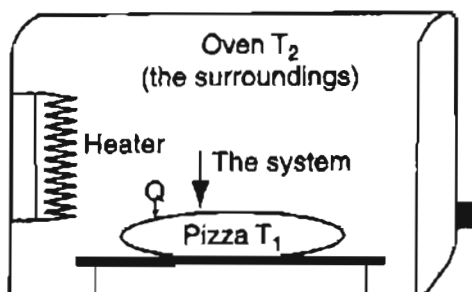


Figure 21.3 Heat transfer is energy crossing the system boundary because of a temperature difference.

Some misconceptions about heat you should avoid (saying heat *transfer* helps) are:

- heat is a substance
- heat is proportional to temperature
- a cold body contains no heat
- heating always results in an increase in temperature
- heat only travels upward

Heat transfer is usually classified in three categories: conduction, convection, and radiation. Heat, as is work, is a path function. To evaluate heat transfer *quantitatively*, you must apply the energy balance that is introduced in Chapter 22, or use an empirical formula to estimate the heat transfer. One example of such a formula is the rate of heat transfer by convection that can be calculated from

$$\dot{Q} = UA(T_2 - T_1) \quad (21.2)$$

where \dot{Q} is the rate of heat transfer (such as J/s), A is the area for heat transfer (such as m^2), $(T_2 - T_1)$ is the temperature difference between the surroundings at T_2 and the system at T_1 (such as $^{\circ}\text{C}$), and U is an empirical coefficient determined from experimental data for the equipment involved [it would have the units of $\text{J}/(\text{s})(\text{m}^2)(^{\circ}\text{C})$]. Recall that in this text we use the symbol \dot{Q} to denote the total amount of heat transferred in a time interval, and not the rate of heat transfer, hence \dot{Q} would have to be summed or integrated to get Q . For example, ignoring conduction and radiation, the convective heat transfer rate from a person (the system) to a room (the surroundings) can be calculated using $U = 7 \text{ W}/(\text{m}^2)(^{\circ}\text{C})$ and the data in Figure 21.4.

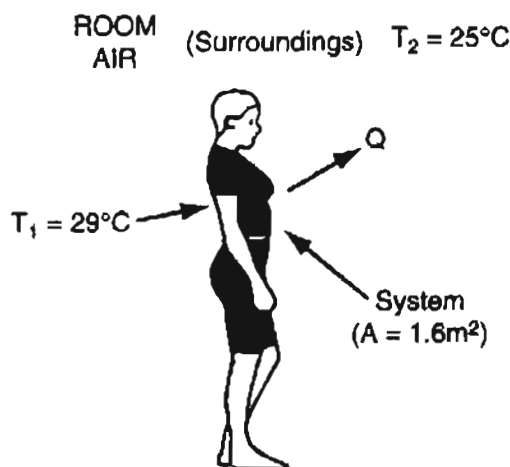


Figure 21.4 Heat transfer from a person.

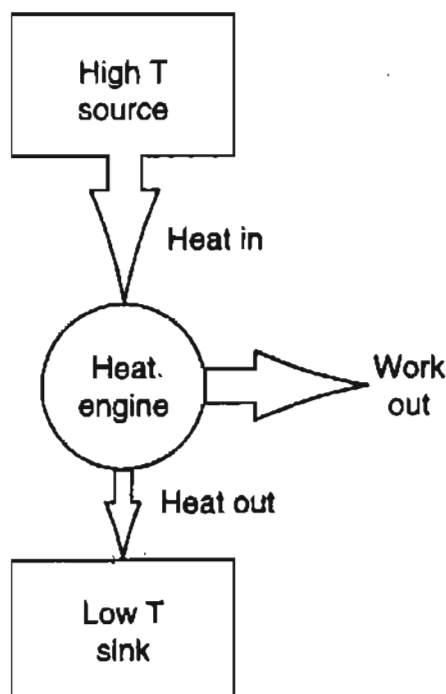


Figure 21.5 A heat engine produces work by operating between a high temperature fluid and a low temperature fluid.

$$\dot{Q} = \frac{7\text{W}}{(\text{m}^2)(^\circ\text{C})} \left| \frac{1.6\text{ m}^2}{(25 - 29)^\circ\text{C}} \right| = -44.8\text{ W or } -44.8\text{ J/s}$$

Multiply \dot{Q} by the time period to get Q in watt hours. What is the value of the rate of heat transferred into the air if the air is the system? It is $+44.8\text{W}$.

A device (system) that uses a high temperature fluid and a low temperature fluid to do work is known as a “heat engine.” Examine Figure 21.5. Examples are power plants, steam engines, heat pumps, and so on.

SELF-ASSESSMENT TEST

Questions

1. There can be no heat transfer between two systems that are at the same temperature. True or false?
2. Which of the following are valid terms for heat transfer:
 - heat addition
 - heat rejection
 - heat absorption
 - heat gain
 - heat loss
 - heat of reaction
 - specific heat
 - heat generation
 - heat storage
 - electrical heating
 - resistance heating
 - frictional heating
 - gas heating
 - waste heat

- heat content
- heat quality
- heat sink
- body heat
- process heat
- heat source

3. Which of the following statements present an incorrect view of heat:
- a. Los Angeles winters are mild because the ocean holds a lot of heat.
 - b. Heat rises in a chimney of a fireplace.
 - c. Your house won't lose much heat this winter because of the new insulation in the attic.
 - d. A nuclear power plant dumps a lot of heat into the river.
 - e. Close that door—don't let the heat out (in Minnesota) or in (in Texas).

Problems

1. A calorimeter (a device to measure heat transfer) is being tested. It consists of a sealed cylindrical vessel containing water placed inside a sealed, well-insulated tank containing ice water at 0°C . The water in the cylinder is heated by an electric coil so that 1000 J of energy are introduced into the water. Then the water is allowed to cool until it reaches 0°C after 15 minutes and is in thermal equilibrium with the water in the ice bath.
 - a. How much heat was transferred from the ice bath to the surrounding air during this test?
 - b. How much heat was transferred from the cylinder to the ice bath during the test?
 - c. If you pick two different systems comprised of (a) the ice bath and (b) the cylinder, was the heat transfer to the ice bath *exactly* the same as the heat transfer from the ice bath to the cylinder?
 - d. Is the interaction between the surroundings and the ice chest work, heat, or both?
2. Classify the energy transfer in the following processes as (a) work, (b) heat, (c) both, or (d) neither.
 - a. A gas in a cylinder is compressed by a piston, and as a result the temperature of the gas rises. The gas is the system.
 - b. When an electric space heater is operating in a room, the temperature of the air goes up. The system is the room.
 - c. The same situation as in (b) but the system is the space heater.
 - d. The temperature of the air in a room increases because of the sunshine passing through a window.

Thought Problems

1. A piece of metal and a piece of wood are at the same temperature, yet the metal feels colder than the wood. Why?
2. The freezing point and the melting point of a substance are at the same temperature. If you put a piece of the solid into the liquid, why does it not melt? The ability to walk barefoot across a bed of red-hot embers has long been a sign of supernatural powers, and recently a demonstration of confidence-raising. How can a person walk across the embers and not be injured?

3. Suppose you place a jar three-quarters full of water in a pot that rests on a stove burner. Place the jar on an upside down saucer in the bottom of the pot. Then fill the pot with water up to the same level as the water in the jar. Heat the water in the pot so that it boils. Why will the water in the jar not boil?

Discussion Problems

1. Worldwide interest exists in the possible global warming that occurs as a result of man's activities. Prepare a report with tables that lists the sources of and mitigation options that exist for total CO_2 , CH_4 , CFC, and NO_2 emissions in the world. For example, for CH_4 include rice cultivation, enteric fermentation, landfills, and so on. If possible, find data for the values of the annual emissions in Mt/yr. For the mitigation options, list the possible addition approximate costs over current cost to implement the option per 1 ton of emitter.
2. What are some of the major steps to take in reducing heat loss from a house?
3. In one of the explanations of the energy balance, the question was posed "Why do you not burn your hand when you put it into the oven at 300°C , but burn it if you touch the metal tray in the oven?" The answer was

There are two important reasons. First, the mass of air surrounding the hand is very small (the density of air at 300°C and 1 atm is 0.615 kg/m^3), and hence its heat content is small despite the high oven temperature. Second, the air is a poor conductor and the relatively still hot air will not burn.

The metal oven tray, on the other hand, has a much larger mass and hence contains much more heat than the air. In addition, the metals are better conductors of heat. Therefore, a good conductor coupled to a large reservoir of heat will relay large quantities of heat at a faster rate than blood can take it away from the fingers.

Comment on the answer; tell what aspects are right and are wrong with it.

4. The following letter appeared in *The Physics Teacher*, October 1990, p. 441:

The recent article on "The Meaning of Temperature" by R. Baierlein is interesting but I believe it fails in its purpose. Baierlein quotes Eric Rogers' definition that "temperature is hotness measured in some definite scale." I very much admired Eric Rogers and this definition, coupled with his statement that "heat is something that makes things hotter, or melts solids, or boils away liquids" might be adequate for the layman. But in no way are they acceptable scientific definitions. Similarly, Baierlein's statement that "hotness is the tendency to transfer energy in irregular, microscopic fashion" and his conclusion that "the function of temperature . . . is to tell us about a system's tendency to transfer energy (as heat)" are not only vague and nonoperational, but they are also incorrect or at least misleading.

- (a) Would you agree with these statements?
- (b) Read the complete letter and Baierlein's reply in *The Physics Teacher*, and prepare a one-page summary of your views on the relation of temperature and heat transfer.
- (c) Also read Octave Levenspiel's amusing discussion of thermometry in *Chemical Engineering Education*, Summer 1975, pp. 102–105, for a different viewpoint.

We next discuss three types of energy that can be stored, that is, retained because material has associated energy: kinetic energy, potential energy, and internal energy.

21.2-3 Kinetic Energy

Kinetic energy (KE) is the energy a system, or some material, possesses because of its velocity relative to the surroundings, which are usually, *but not always*, at rest. The wind, moving automobiles, waterfalls, flowing fluids, and so on, possess kinetic energy. The kinetic energy of a material refers to what is called the macroscopic kinetic energy, namely the energy that is associated with the gross movement (velocity) of the system or material, and not the kinetic energy of the individual molecules that belong in the category of internal energy that is discussed in Section 21.2-5 below.

Do you recall the equation used to calculate the kinetic energy relative to stationary surroundings? It is

$$KE = \frac{1}{2}mv^2 \quad (21.3a)$$

for the kinetic energy or

$$\widehat{KE} = \frac{1}{2}v^2 \quad (21.3b)$$

for the specific kinetic energy where the superscript caret (^) refers to the energy per unit mass and not the total kinetic energy, as in Equation 21.3a. In Equation (21.3a), m refers to the center of mass of the material and v to a suitably averaged velocity of the material. The value of a *change* in the specific kinetic energy ($\Delta\widehat{KE}$) occurs in a specified time interval, and depends only on the mass and the initial and final values of the velocity of the material.

EXAMPLE 21.2 Calculation of the Specific Kinetic Energy for a Flowing Fluid

Water is pumped from a storage tank through a tube of 3.00 cm inner diameter at the rate of 0.001 m³/s. See Figure E21.2 What is the specific kinetic energy of the water in the tube?

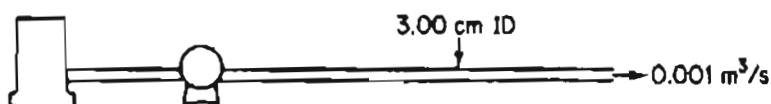


Figure E21.2

Solution

Basis: 0.001 m³/s of water

$$\text{Assume that } \rho = \frac{1000 \text{ kg}}{\text{m}^3} \quad r = \frac{1}{2} (3.00) = 1.50 \text{ cm}$$

$$v = \frac{0.001 \text{ m}^3}{\text{s}} \left| \frac{1}{\pi (1.50)^2 \text{ cm}^2} \right| \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 = 1.415 \text{ m/s}$$

$$\widehat{KE} = \frac{1}{2} \left| \left(\frac{1.415 \text{ m}}{\text{s}} \right)^2 \right| \left| \frac{1(\text{N})(\text{s}^2)}{1(\text{kg})(\text{m})} \right| \left| \frac{1 \text{ J}}{1(\text{N})(\text{m})} \right| = 1.00 \text{ J/kg}$$

SELF-ASSESSMENT TEST**Questions**

1. Can the kinetic energy of a mass be zero if the mass has a velocity, that is, is moving?
2. Temperature is a measure of the average kinetic energy of a material. True or false?
3. The kinetic energy of an automobile going 100 miles/hr is greater than the energy stored in the battery of the automobile (300 Wh). True or false?

Problem

1. Calculate the kinetic energy change in the water that occurs when 10,000 lb/hr flow in a pipe that is reduced from a diameter of 2 in. to a diameter of 1 in.

21.2-4 Potential Energy

Potential energy (*PE*) is energy the system possesses because of the force exerted on its mass by a gravitational or electromagnetic field with respect to a reference surface. When an electric car or bus goes uphill it gains potential energy (Figure 21.6), energy that can be recovered to some extent by regeneration—charging the batteries if needed when the automobile goes down the hill on the other side. You can calculate the potential energy in a gravitational field from

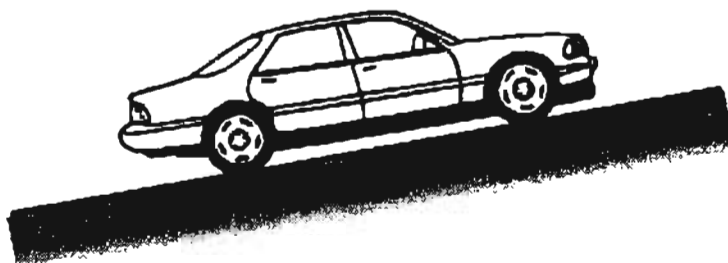


Figure 21.6 Gain of potential energy by an electric automobile going uphill.

$$PE = mgh \quad (21.4a)$$

or the specific potential energy

$$\widehat{PE} = gh \quad (21.4b)$$

where h is the distance from the reference surface and the symbol (\wedge) again means potential energy per unit mass. The measurement of h takes place to the center of mass of a system. Thus, if a ball suspended inside a container somehow is permitted to drop from the top of the container to the bottom, and in the process raises the thermal energy of the system slightly, we do not say work is done on the system but instead say that the potential energy of the system is reduced (slightly). The value of a *change* in the specific potential energy, $\Delta\widehat{PE}$, occurs in a specified time interval, and depends only on the initial and final states of the system (state variable), and not on the path followed.

EXAMPLE 21.3 Calculation of Potential Energy Change of Water

Water is pumped from one reservoir to another 300 ft away, as shown in Figure E21.3. The water level in the second reservoir is 40 ft above the water level of the first reservoir. What is the increase in specific potential energy of the water in Btu/lb_m?

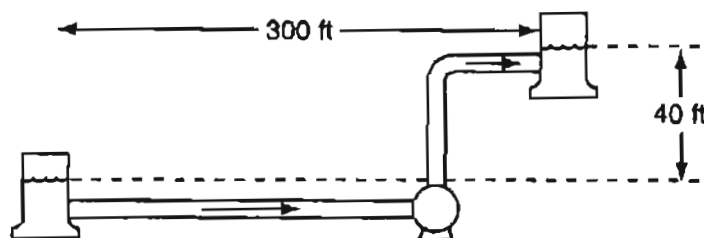


Figure E21.3

Solution

Because you are asked to calculate the potential energy change of one pound of water and not of the whole reservoir, which would require knowledge of the mass of water in the reservoir, you can assume that the 40 ft corresponds to the difference in height of the one pound of water when it is pumped from one level to the other level. Think of a ping-pong ball riding on top of the water.

Let the water level in the first reservoir be the reference plane. Then $h = 40$ ft.

$$\Delta\widehat{PE} = \frac{32.2 \text{ ft}}{\text{s}^2} \left| \frac{(40 - 0) \text{ ft}}{32.2 \text{ (lb}_m\text{)(ft)}} \right| \frac{1 \text{ (lb}_f\text{)(s}^2\text{)}}{32.2 \text{ (lb}_m\text{)(ft)}} \frac{1 \text{ Btu}}{778.2 \text{ (ft)(lb}_f\text{)}} = 0.0514 \text{ Btu/lb}_m$$

SELF-ASSESSMENT TEST

Questions

1. Answer the following questions true or false:
 1. Potential energy has no unique absolute value.
 2. Potential energy can never be negative.
 3. The attractive and repulsive forces between the molecules in a material contribute to the potential energy of a system.
2. The units of potential energy or kinetic energy in the American Engineering System are (select all the correct expressions):
 - a. $(\text{ft})(\text{lb}_f)$
 - b. $(\text{ft})(\text{lb}_m)$
 - c. $(\text{ft})(\text{lb}_f)/(\text{lb}_m)$
 - d. $(\text{ft})(\text{lb}_m)/(\text{lb}_f)$
 - e. $(\text{ft})(\text{lb}_f)/(\text{hr})$
 - f. $(\text{ft})(\text{lb}_m)/(\text{hr})$

Problems

1. A 100-kg ball initially at rest on the top of a 5-m ladder is dropped and hits the ground. With reference to the ground:
 - a. What are the initial kinetic and potential energy of the ball?
 - b. What are the final kinetic and potential energy of the ball?
 - c. What are the changes in kinetic and potential energy for the process?
 - d. If all the initial potential energy were somehow converted to heat, how many calories would this amount to? How many Btu? How many joules?
2. A 1 kg ball 10 m above the ground is dropped and hits the ground. What is the change in PE of the ball?

Thought Problem

1. Why does a bicyclist pick up speed when going downhill even if he or she is not pedaling. Doesn't this situation violate the conservation of energy concept?

21.2-5 Internal Energy

Internal energy (U) is a *macroscopic* concept that takes into account all of the molecular, atomic, and subatomic energies, all of which follow definite microscopic conservation rules for dynamic systems. Internal energy can be stored. Because no instruments exist with which to measure internal energy directly on a macroscopic scale, internal energy must be calculated from certain other variables that can be measured macroscopically, such as pressure, volume, temperature, and composition.

To calculate the internal energy per unit mass (\hat{U}) from the variables that can be measured, we make use of a special property of internal energy, namely that it is an exact differential because it is a *point* or *state variable*, as described previously in Section 21.1. For a pure component, \hat{U} can be expressed in terms of just two intensive variables according to the phase rule for one phase:

$$\mathcal{F} = 2 - \mathcal{P} + C = 2 - 1 + 1 = 2$$

Custom dictates the use of temperature and specific volume as the two variables. For a *single phase* and single component, we say that \hat{U} is a function of T and \hat{V}

$$\hat{U} = \hat{U}(T, \hat{V})$$

By taking the total derivative, we find that

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T} \right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}} \right)_T d\hat{V} \quad (21.5)$$

By definition $(\partial \hat{U} / \partial T)_{\hat{V}}$ is the “**heat capacity**” (specific heat) at constant volume, given the special symbol C_V . C_V can also be defined to be the amount of heat necessary to raise the temperature of one kilogram of substance by one degree in a closed system, and so has the SI units of J/(kg)(K), if the process is carried out at constant volume. We discuss how to get numerical values for heat capacities in Chapter 23. For all practical purposes in this text, the term $(\partial \hat{U} / \partial \hat{V})_T$ is so small that the second term on the righthand side of Equation (21.5) can be neglected. Consequently, *changes in the specified internal energy* over a specified time interval can be computed by integrating Equation (21.5) as follows:

$$\Delta \hat{U} = \hat{U}_2 - \hat{U}_1 = \int_{\hat{U}_1}^{\hat{U}_2} d\hat{U} = \int_{T_1}^{T_2} C_V dT \quad (21.6)$$

For an ideal gas U is a function of temperature only. Equation (21.6) alone is *not* valid if a phase change occurs during the process.

Note that you can only calculate differences in internal energy, or calculate the internal energy relative to a reference state, *but not absolute values* of internal energy. Look up the values of p and \hat{V} for water for the reference state that has been assigned a zero value for \hat{U} . In the SI tables did you get $p = 0.6113$ kPa, and for liquid water, $\hat{V} = 0.001000$ m³/kg? The reference internal energy cancels out when you calculate an internal energy difference

$$\Delta \hat{U} = (\hat{U}_2 - \hat{U}_{\text{ref}}) - (\hat{U}_1 - \hat{U}_{\text{ref}}) = \hat{U}_2 - \hat{U}_1 \quad (21.7)$$

What would be the value for $\Delta \hat{U}$ for a constant volume system if 1 kg of water at 100 kPa was heated from 0°C to 100°C, and then cooled back to 0°C and 100 kPa? Would $\Delta \hat{U} = 0$? Yes, because it is a state variable, and the integral in Equation (21.6) would be zero because $\hat{U}_2 = \hat{U}_1$.

The internal energy of a system containing more than one component is the sum of the internal energies of each component

$$U_{\text{tot}} = m_1 \hat{U}_1 + m_2 \hat{U}_2 + \cdots + m_n \hat{U}_n \quad (21.8)$$

The heat of mixing (discussed in Chapter 28) is neglected in Equation (21.8).

If a phase change occurs in the system that you are analyzing, the internal energy change of the phase change must be taken into account, as will be explained in Chapter 23. How to take into account the internal energy change when chemical reactions occur is covered in Chapter 25.

EXAMPLE 21.4 Calculation of an Internal Energy Change Using the Heat Capacity

What is the change in internal energy when 10 kg mol of air is cooled from 60°C to 30°C in a constant volume process?

Solution

Since you don't know the value of C_V , you have to look the value up. It is $2.1 \times 10^4 \text{ J/(kg mol)(}^\circ\text{C)}$ over the temperature range. Use Equation (21.6) to carry out the calculation:

$$\begin{aligned}\Delta U &= 10 \text{ kg mol} \int_{60^\circ\text{C}}^{30^\circ\text{C}} \left(2.1 \times 10^4 \frac{\text{J}}{(\text{kg mol})(^\circ\text{C})} \right) dT = 2.1 \times 10^5 (30 - 60) \\ &= -6.3 \times 10^6 \text{ J}\end{aligned}$$

EXAMPLE 21.5 Calculation of the Change in Internal Energy by Different Paths

Figure E21.5 illustrates two different possible paths taken by a gas in a process. For which path will $\Delta \hat{U}$ be the greatest, Path A or Path B?

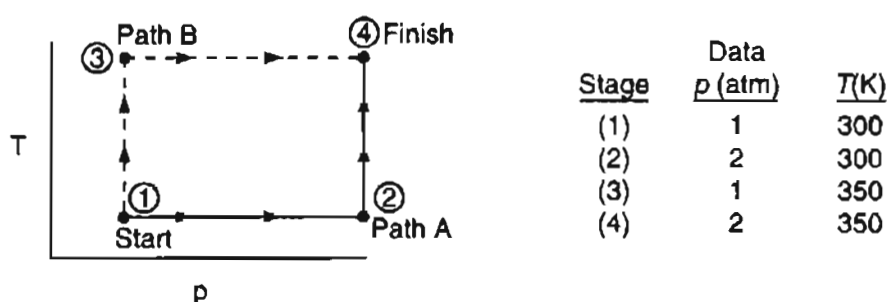


Figure E21.5

Solution

Because \hat{U} is a state (point) variable, $\Delta \hat{U}$ depends only on the initial and final conditions, and not the path between (1) and (4). Hence, the answer is there is no difference in $\Delta \hat{U}$ between Path A and Path B.

SELF-ASSESSMENT TEST

Questions

1. An entrance examination for graduate school asked the following two multiple-choice questions:
 - a. The internal energy of a solid is equal to the
 - (1) absolute temperature of the solid
 - (2) total kinetic energy of its molecules
 - (3) total potential energy of its molecules
 - (4) sum of the kinetic and potential energy of its molecules
 - b. The internal energy of an object depends on its
 - (1) temperature, only
 - (2) mass, only
 - (3) phase, only
 - (4) temperature, mass, and phaseWhich answers would you choose?
2. If C_V is not constant over the temperature range in Equation (21.6), can you still integrate C_V to get ΔU ?

Problems

1. A database lists an equation for \hat{U} as

$$\hat{U} = 1.10 + 0.810T + 4.75 \times 10^{-4} T^2$$

where \hat{U} is in kJ/kg and T is in °C. What is (a) the corresponding equation for C_V ? (b) the reference temperature for \hat{U} ?

2. Use the steam tables to calculate the change in internal energy change between liquid water at 1000 kPa and 450 K, and steam at 3000 kPa and 800 K. How did you account for the phase change in the water?

Thought Problem

1. Are there any reasons why internal energy should be used in your calculations when most problems seem to involve open systems?

Discussion Problems

1. Richard Feynman was a brilliant physicist and comedian who invested a great amount of effort in making physics accessible to students. In one of his lectures he wrote: "Let us consider a rubber band. When we stretch the rubber band, we find that its temperature _____." Fill in the missing word for the professor.
2. Would you say it is better to use a photovoltaic system of solar collectors to heat a swimming pool, or to use water heated by a thermal solar collector?

21.2-6 Enthalpy

You will find in Chapter 22 and subsequent chapters that the term $U + pV$ (or $\hat{U} + p\hat{V}$ per unit mass or mole) occurs repeatedly in an energy balance. The combined variables are called the **enthalpy** (pronounced en-*thal*-py).

$$H = U + pV \quad (21.9a)$$

where p is the pressure and V is the volume, or per unit mass or mole

$$\hat{H} = \hat{U} + p\hat{V} \quad (21.9b)$$

To calculate the specific enthalpy (enthalpy per unit mass), as with the internal energy, we use the property that the enthalpy is an exact differential. As you saw for internal energy, the state for the enthalpy for a **single phase** and single component can be completely specified by two intensive variables. We will express the enthalpy in terms of the temperature and pressure (a more convenient variable than the specific volume). If we let

$$\hat{H} = \hat{H}(T, p)$$

by taking the total derivative of \hat{H} we can form an expression analogous to Equation (21.5):

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T} \right)_p dT + \left(\frac{\partial \hat{H}}{\partial p} \right)_T dp \quad (21.10)$$

By definition $(\partial \hat{H} / \partial T)_p$ is the heat capacity at constant pressure, and is given the special symbol C_p . For most practical purposes $(\partial \hat{H} / \partial p)_T$ is so small at modest pressures that the second term on the righthand side of Equation (21.10) can be neglected. Changes in enthalpy over a specified time interval can then be calculated by integration of Equation (21.10) as follows:

$$\Delta \hat{H} = \hat{H}_2 - \hat{H}_1 = \int_{\hat{H}_1}^{\hat{H}_2} d\hat{H} = \int_{T_1}^{T_2} C_p dT \quad (21.11)$$

However, in processes operating at high pressures, the second term on the righthand side of Equation (21.10) cannot necessarily be neglected, but must be evaluated from experimental data. Consult the references at the end of the chapter for details. Equation (21.11) is *not* valid if a phase change occurs. One property of ideal gases, but *not* of real gases, should be noted, namely that their enthalpies and internal energies are functions of temperature only, and are not influenced by changes in pressure or specific volume.

The enthalpy of a system containing more than one component is the sum of the enthalpies of each component.

$$H_{\text{tot}} = m_1 \hat{H}_1 + m_2 \hat{H}_2 + \cdots + m_n \hat{H}_n \quad (21.12)$$

The heat of mixing (discussed in Chapter 28) is neglected in Equation (21.12).

As with internal energy, **enthalpy has no absolute value; only changes in enthalpy can be calculated.** Often you will use a reference set of conditions (perhaps implicitly) in computing enthalpy changes. For example, the reference conditions used in the steam tables are liquid water at 0°C (32°F) and its vapor pressure. This does not mean that the enthalpy is actually zero under these conditions, but merely that the enthalpy has arbitrarily been assigned a value of zero at these conditions. In computing enthalpy changes, the reference conditions cancel out, as can be seen from the following:

<i>Initial state of system (1)</i>	<i>Final state of system (2)</i>
enthalpy = $\hat{H}_1 - \hat{H}_{\text{ref}}$	enthalpy = $\hat{H}_2 - \hat{H}_{\text{ref}}$
net enthalpy change = $(\hat{H}_2 - \hat{H}_{\text{ref}}) - (\hat{H}_1 - \hat{H}_{\text{ref}}) = \hat{H}_2 - \hat{H}_1$	

EXAMPLE 21.6 Calculation of the Change in Enthalpy by Two Different Paths

Figure E21.6 illustrates the change in the state of a gas from A to D by two paths. Will $\Delta \hat{H}$ be greater by going via route A-B-D or by A-C-D from point A to point D?

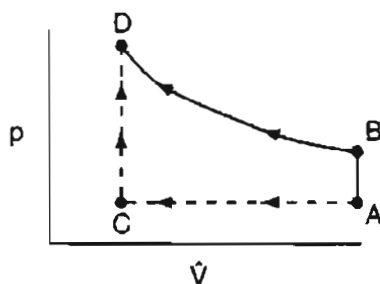


Figure E21.6

Solution

Because \hat{H} is a state (point) variable, only the beginning and ending conditions are involved in calculating $\Delta \hat{H}$. Consequently, the answer is both paths will result in the same value of $\Delta \hat{H}$.

If a phase change occurs in the system that you are analyzing, the enthalpy of the phase change must be taken into account, as explained in Chapter 23. How to take into account chemical reactions is explained in Chapter 25.

EXAMPLE 21.7 Calculation of an Enthalpy Change

Calculate the enthalpy change for the process in Example 21.4, except assume that the enthalpy change occurs in a constant pressure, steady-state flow process.

Solution

For the example you have to look up the value of C_p . It is 2.9×10^4 J/(kg mol)(°C). Use Equation (21.11) to carry out the calculation:

$$\begin{aligned}\Delta H &= 10 \text{ kg mol} \int_{60^\circ\text{C}}^{30^\circ\text{C}} (2.9 \times 10^4) \frac{\text{J}}{(\text{kg mol})(^\circ\text{C})} dT = 2.9 \times 10^5 (30 - 60) \\ &= -8.7 \times 10^6 \text{ J}\end{aligned}$$

Although you have probably learned from chemistry that for an ideal gas

$$C_p = C_v + R$$

sometimes books say to neglect the difference between C_p and C_v for solids and liquids. But you can see from the following list that you should look up the respective values rather than rely on an approximation

	J/(g mol) (°C)	
	C_p	C_v
CH ₃ OH (ℓ)	80.4	62.8
CCl ₄ (ℓ)	128.1	88.0
NaCl (s)	50.3	47.8

SELF-ASSESSMENT TEST

Questions

- When you read in the steam table in two adjacent columns that $\hat{U} = 4184$ J and $\hat{H} = 4184$ J, is the water liquid or vapor?
- Repeat 1 for $\hat{U} = 1362$ J and $\hat{H} = 1816$ J.

Problems

1. The enthalpy change of a real gas can be calculated from

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT + \int_{p_1}^{p_2} \left[\hat{V} - T \left(\frac{\partial \hat{V}}{\partial T} \right)_p \right] dp$$

What is the enthalpy change for a real gas in

- an isothermal process
 - an isochoric (constant volume) process
 - an isobaric process
2. Will the enthalpy change be greater along the path shown in Figure SAT 21.2P2b by the solid line or by the path shown by the dashed line?

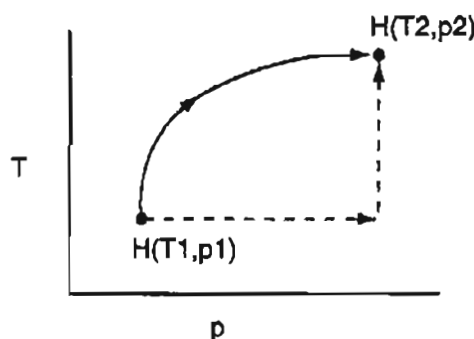


Figure SAT 21.2P2b

3. Show that for an incompressible ($d\hat{V} = 0$) liquid or solid that

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p dT + \hat{V}(p_2 - p_1)$$

Discussion Problems

- How did the name enthalpy become attached to the sum of U plus (pV) ?
- Is the enthalpy change of a real gas undergoing a process the enthalpy change of each of the individual molecules comprising the gas?

Looking Back

In this chapter we described much of the terminology essential to your understanding of energy balances. Then we discussed the six main types of energy incorporated in the energy balance: work, heat, kinetic energy, potential energy, internal energy, and enthalpy.

GLOSSARY OF NEW WORDS

Adiabatic A system that does not exchange heat with the surroundings during a process.

Adiabatic process A process in which no heat transfer occurs ($Q = 0$).

Boundary Hypothetical perimeter used to define what the system is.

Closed system A system in which mass is not exchanged with the surroundings.

Electric work Work done on or by a system because a voltage difference forces a current to flow.

Energy The capacity to do work or transfer heat.

Energy transfer The movement of energy from one site or state to another.

Enthalpy (H) The sum of the variables $U + pV$.

Equilibrium state The properties of the system remain invariant under a balance of potentials.

Extensive property A property that depends on the amount of material present, such as volume, mass, etc.

Flow system See Open system.

Flow work Work done on the system to put a fluid element into the system, or work done by the system to push a fluid element into the surroundings.

Heat (Q) Energy transfer across a system boundary that is caused by a temperature difference (potential) between the system and the surroundings.

Heat capacity Also called the specific heat. One heat capacity, C_v , is defined as the change in internal energy with respect to temperature at constant volume, and a second heat capacity, C_p , is defined as the change in enthalpy with respect to temperature at constant pressure.

Intensive property A property that is independent of the amount of material present, such as temperature, pressure, or any specific variable (per unit amount of material, mass, or mole).

Internal energy (U) Energy that represents a macroscopic account of all of the molecular, atomic, and subatomic energies, all of which follow definite microscopic conservation rules for dynamic systems.

Isobaric A system for which the pressure is invariant during a process.

Isochoric A system for which the volume is invariant during a process.

Isothermal A system in which the temperature is invariant during a process.

Kinetic energy (KE) Energy a system possesses because of its velocity relative to the surroundings.

Nonflow system See Closed system.

Open system A system in which interchange of mass occurs with the surroundings.

Path variable (function) A variable (function) whose value depends on how the process takes place, such as heat and work.

Point function See State variable

Potential energy (PE) Energy the system possesses because of the force exerted on its mass by a gravitational or electromagnetic field with respect to a reference surface.

Power Work per unit time.

Property An observable or calculable characteristic of a system, such as temperature or enthalpy.

Shaft work Work corresponding to a force acting on a shaft to turn it.

Single phase A part of the system that is physically distinct and homogeneous, as for example a gas or liquid.

State Condition of the system, such as the value of the temperature, pressure, etc.

State variable (function) A variable (function), also called a point function, whose value depends only on the state of the system and not upon its previous history. An example is internal energy.

Steady state The accumulation in the system is zero, the flows in and out are constant, and the properties of the system are invariant.

Surroundings Everything outside the system.

System The quantity of matter or region of space chosen for analysis.

Transient See Unsteady state.

Unsteady state Not steady state (see Steady state).

Work (W) Work is a form of energy that represents a transfer of energy between the system and surroundings.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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PROBLEMS

- *21.1 Convert 45.0 Btu/lb_m to the following:
 (a) cal/kg (b) J/kg
 (c) kWh/kg (d) (ft)(lb_f)/lb_m
- *21.2 Convert the following physical properties of liquid water at 0°C and 1 atm from the given SI units to the equivalent values in the listed American Engineering units.
 (a) Heat capacity of 4.184 J/(g)(K) Btu/(lb)(°F)
 (b) Enthalpy of -41.6 J/kg Btu/lb
 (c) Thermal conductivity of 0.59 (kg)(m)/(s³)(K) Btu/(ft)(hr)(°F)
- *21.3 Convert the following quantities as specified.
 (a) A rate of heat flow of 6000 Btu/(hr)(ft²) to cal/(s)(cm²).
 (b) A heat capacity of 2.3 Btu/(lb)(°F) to cal/(g)(°C)
 (c) A thermal conductivity of 200 Btu/(hr)(ft)(°F) to J/(s)(cm)(°C).
 (d) The gas constant, 10.73 (psia)(ft³)/(lb mol)(°R) to J/(g mol)(K).
- *21.4 A simplified equation for the heat transfer coefficient from a pipe to air is

$$h = \frac{0.026G^{0.6}}{D^{0.4}}$$

where h = heat transfer coefficient, Btu/(hr)(ft²)(°F)

G = mass rate flow, lb_m/(hr)(ft²)

D = outside diameter of the pipe, (ft)

If h is to be expressed in J/(min)(cm²)(°C), and the units of G and D remain the same, what should the new constant in the equation be in place of 0.026?

- *21.5** A problem for many people in the United States is excess body weight stored as fat. Many people have tried to capitalize on this problem with fruitless weight-loss schemes. However, since energy is conserved, an energy balance reveals only two real ways to lose weight (other than water loss): (1) reduce the caloric intake, and/or (2) increase the caloric expenditure. In answering the following questions, assume that fat contains approximately 7700 kcal/kg (1 kcal is called a "dietetic calorie" in nutrition, or commonly just a "Calorie").
- If a normal diet containing 2400 kcal/day is reduced by 500 kcal/day, how many days does it take to lose 1 lb of fat?
 - How many miles would you have to run to lose 1 lb of fat if running at a moderate pace of 12 km/hr expends 400 kJ/km?
 - Suppose that two joggers each run 10 km/day. One runs at a pace of 5 km/hr and the other at 10 km/hr. Which will lose more weight (ignoring water loss)?
- *21.6** The energy from the sun incident on the surface of the earth averages 32.0 cal/(min)(cm²). It has been proposed to use space stations in synchronous orbits 36,000 km from earth to collect solar energy. How large a collection surface is needed (in m²) to obtain 10⁸ watts of electricity (equivalents to a 100 MW power plant)? Assume that 10% of the collected energy is converted to electricity. Is your answer a reasonable size?
- *21.7** Solar energy has been suggested as a source of renewable energy. If in the desert the direct radiation from the sun (say for 320 days) is 975 W/m² between 10 AM and 3 PM, and the conversion efficiency to electricity is 21.0%, how many square meters are needed to collect an amount of energy equivalent to the annual U.S. energy consumption of 3×10^{20} J? Is the construction of such an area feasible?
- How many tons of coal (of heating value of 10,000 Btu/lb) would be needed to provide the 3×10^{20} J if the efficiency of conversion to electricity was 70%? What fraction of the total U.S. resources of coal (estimated at 1.7×10^{12} tons) is the calculated quantity?
- *21.8** Lasers are used in many technologies, but they are fairly large devices even in CD players. A materials scientist has been working on producing a laser from a microchip. He claims that his laser can produce a burst of light with up to 10,000 watts, qualifying it for use in eye surgery, satellite communications, and so on. Is it possible to have such a powerful laser in such a small package?
- *21.9** The thermal conductivity equation for a substance is

$$k = a + bT$$

where k is in (Btu)/(hr) (ft)(°F)

T is temperature, °F

a , b are constants with appropriate units.

Convert the above relation to make it possible to introduce the temperature into the modified equation as °C, and to have the units in which k is expressed be (J)/(min)(cm)(K). Your answer should be the modified equation. Show all transformations.

- *21.10** In an electric gun, suppose we want the muzzle velocity to be Mach 4, or about 4,400 ft/sec. This is a reasonable number because around 3,500 ft/sec you begin to start getting hypervelocity effects, like straws going through doors.

Now the requirement that our slug start from zero and reach 4,400 ft/sec in 20 feet exactly defines our environment, if we insist that the acceleration is constant, which is a good starting point.

By a simple manipulation of Newton's Laws, we find that the time of launch is 9 milliseconds. If the slug weighs a kilogram, which is much less than a tank shell, but quite sufficient to wreck any tank it hits at Mach 4, then the kinetic energy of the bullet is 900,000 joules. Since we have 9 ms to get this energy into the slug, we have to transfer about 100 megawatts into the bullet during the 9 ms launch time.

Is the energy transfer really 100 MW?

- **21.11** A letter to the editor of the local newspaper said:

Q. I'm trying to eat a diet that's less than 30 percent fat. I bought some turkey franks advertised as "80 percent fat free."

The statistical breakdown on the back of the package shows each frank has 8 grams of fat and 100 calories. If a gram of fat has nine calories, that makes the frank have about 75 percent fat. I'm so confused; is it them or is it me?

How would you answer the question?

- *21.12** How much weight can you loose by exercise, say running?

Data: 1 kg fat = 7700 Calories = 7700 kg cal = 32,000 J

Running at 5 min/km requires the expenditure of about 400 kJ/km.

- *21.13** An overweight person decides to loose weight by exercise. Hard aerobic exercise requires 700 W. By exercising for one-quarter of an hour, can the person compensate for a big meal (4000 kJ)?

- *21.14** Answer the following question true or false:

- A simple test to determine if a property is an extensive property is to split the system in half, and if the value of the sum of the properties in each half is twice the value of the property in one half, then the property is an extensive variable.
- The value of a state variable (point function) depends only on its state and not how the state was reached.
- An intensive variable is a variable whose value depends on the amount of mass present.
- Temperature, volume, and concentration are intensive variables.
- Any variable that is expressed as a "specific", i.e., per unit mass, quantity is deemed to be an intensive variable.

- *21.15** Answer the following questions true or false:

- An isobaric process is one of constant pressure.
- An isothermal process is one of constant temperature.
- An isometric process is one of constant volume.
- A closed system is one in which mass does not cross the system boundary.
- The units of energy in the SI system are joules.

- (f) The units of energy in the AE system can be $(\text{ft})(\text{lb}_f)/\text{lb}_m$.
 (g) The difference between an open system and a closed system is that energy transfer can take place between the system and the surrounding in the former but not in the later.

21.16* Are the following variables intensive or extensive?

- | | |
|----------------------|-------------------------|
| (a) Partial pressure | (e) Relative saturation |
| (b) Volume | (f) Specific volume |
| (c) Specific gravity | (g) Surface tension |
| (d) Potential energy | (h) Refractive index |

***21.17** Classify the following measurable physical characteristics of a gaseous mixture of two components as (1) an intensive property, (2) an extensive property, (3) both, or (4) neither:

- | | |
|-----------------|-----------------|
| (a) Temperature | (c) Composition |
| (b) Pressure | (d) Mass |

***21.18** A can of soda at room temperature is put into the refrigerator so that it will cool. Would you model the can of soft drink as a closed system or as an open system? Explain.

***21.19** Suppose that a constant force of 40.0 N is exerted to move an object for 6.00 m. What is the work accomplished (on an ideal system) expressed in the following:

- | | |
|--------------------------------|---------|
| (a) joules | (c) cal |
| (b) $(\text{ft})(\text{lb}_f)$ | (d) Btu |

***21.20** A gas is contained in a horizontal piston-cylinder apparatus at a pressure of 350 kPa and a volume of 0.02 m^3 . Determine the work done by the piston on the gas if cylinder volume is increased to 0.15 m^3 through heating. Assume the pressure of the gas remains constant throughout the process, and that the process is ideal.

***21.21** A rigid tank contains air at 400 kPa and 600°C . As a result of heat transfer to the surroundings, the temperature and pressure inside the tank drop to 100°C and 200 kPa, respectively. Calculate the work done during this process.

***21.22** A horizontal frictionless piston-cylinder contains 10 lb of liquid water saturated at 320°F . Heat is now transferred to the water until one-half of the water vaporizes. If the piston moves slowly to do work against the surroundings, calculate the work done by the system (the piston-cylinder) during this process.

✓ ***21.23** A horizontal cylinder, closed at one end, is fitted with a movable piston. Originally the cylinder contains 1.2 ft^3 of gas at 7.3 atm pressure. If the pressure against the piston face is reduced very slowly to 1 atm, calculate the work done by the gas on the piston assuming the following relationship to hold for the gas:

$$pV^{1.3} = \text{constant}.$$

***21.24** Answer the following questions true or false:

- The work done by a constant volume system is always zero.
- In a cycle that starts at one state and returns to the same state, the net work done is zero.
- Work is the interchange of energy between the system and its surroundings.

- (d) Work can always be calculated by the integration of $\int p dV$ for a gas.
- (e) For a closed system, the work is always zero.
- (f) When an ideal gas expand in two stages from state one to state two, the first stage being at constant pressure and the second at constant temperature, the work done by the gas is greater during the second stage.
- (g) When positive work is done on a system, its surroundings do an equal quantity of negative work, and vice versa.

***21.25** Often in books you read about "heat reservoirs" existing in two bodies at different temperatures. Can this concept be correct?

***21.26** An examination question asked: "Is heat conserved?" Sixty percent of the students said "no", but 40 percent said "yes". The most common explanation was: (a) "Heat is a form of energy and therefore conserved." The next most common was: (b) "Heat is a form of energy and therefore is not conserved." Two other common explanations were: (c) "Heat is conserved. When something is cooled, it heats something else up. To get heat in the first place, though, you have to use energy. Heat is just one form of energy," and (d) "Yes, heat is transferred from a system to its surroundings and vice versa. The amount lost by one system equals the amount gained by the surroundings." Explain whether or not heat is conserved and criticize each of the four answers.

***21.27** Tell what is right and what is wrong with each of these concepts related to heat:

- (a) Heat is a substance.
- (b) Heat is really not energy.
- (c) Heat and cold are the same thing; they represent opposite end of a continuum.
- (d) Heat and temperature are the same thing.
- (e) Heat is proportional to temperature.
- (f) Heat is not a measurable, quantifiable concept.
- (g) Heat is a medium.
- (h) Heat flows from one object to another, or can be stored.
- (i) Heat is produced by burning.
- (j) Heat cannot be destroyed.

***21.28** This explanation of the operation of a refrigerator was submitted for publication in a professional news magazine:

Recall that in the usual refrigerator, a liquid coolant with a low boiling point vaporizes while at low pressure, absorbing heat from the refrigerator's contents. This heat energy is concentrated by a compressor and the result dissipated in a condenser, with the gas converting to liquid at high pressure. As the liquid passes through an expansion nozzle back into the refrigerator chamber, the cooling cycle begins anew.

Clarify the explanation for the editor of the magazine.

***21.29** Answer the following questions true or false:

- (a) In an adiabatic process no heat transfer occurs.
- (b) When a gas is compressed in a cylinder, no heat transfer occurs.
- (c) If an insulated room contains an operating freezer, no heat transfer takes place if the room is picked as the system.

- (d) Heat and thermal energy are synonymous terms.
- (e) Heat and work are the only mechanisms by which energy can be transferred to a closed system.
- (f) Light is a form of heat.
- (g) You can measure the heat in a system by its temperature.
- (h) Heat is a measure of the temperature of a system.

- *21.30** Calculate the heat transfer to the atmosphere per second from a circular pipe, 5 cm in diameter and 100 m long, carrying steam at an average temperature of 120°C if the surroundings are at 20°C? The heat transfer can be estimated from the relation

$$Q = h A \Delta T$$

where $h = 5 \text{ J/(s)(m}^2\text{)(}^\circ\text{C)}$, A is the surface area of the pipe, and ΔT is the temperature difference between the surface of the pipe and ambient conditions.

- *21.31** Calculate the KE of the liquid flowing in a pipe 5 cm inner diameter at the rate of 500 kg/min. The density of the liquid is 1.15 g/cm³.
- *21.32** Find the kinetic energy in (ft)(lb_f)/(lb_m) of water moving at the rate of 10 ft/s through a pipe 2 in. ID.
- *21.33** A windmill converts the kinetic energy of the moving air into electrical energy at an efficiency of about 30%, depending on the windmill design and speed of the wind. Estimate the power in kW for a wind flowing perpendicular to a windmill with blades 15 m in diameter when the wind is blowing at 20 mi/hr at 27°C and 1 atm.
- *21.34** Before it lands, a vehicle returning from space must convert its enormous kinetic energy to heat. To get some idea of what is involved, a vehicle returning from the moon at 25,000 mi/hr can, in converting its kinetic energy, increase the internal energy of the vehicle sufficiently to vaporize it. Obviously, a large part of the total kinetic energy must be transferred from the vehicle. How much kinetic energy does the vehicle have (in Btu per lb)? How much energy must be transferred by heat if the vehicle is to heat up by only 20°F/lb?
- *21.35** What is the potential energy in joules of a 12 kg mass 25 m above a datum plane?
- *21.36** The world's largest plant that obtains energy from tidal changes is at Saint Malo, France. The plant uses both the rising and falling cycle (one period in or out is 6 hr 10 min in duration). The tidal range from low to high is 14 m, and the tidal estuary (the LaRance River) is 21 km long with an area of 23 km². Assume that the efficiency of the plant in converting potential to electrical energy is 85%, and estimate the average power produced by the plant. (*Note:* Also assume that after high tide, the plant does not release water until the sea level drops 7 m, and after a low tide does not permit water to enter the basin until the level outside the basin rises 7 m, and the level differential is maintained during discharge and charge.)
- *21.37** Find the value of internal energy for water (relative to the reference state) for the states indicated.
- (a) Water at 0.4 MPa, 725°C
 - (b) Water at 3.0 MPa, 0.01 m³/kg
 - (c) Water at 1.0 MPa, 100°C

- ✓**21.38 Calculate the change in the internal energy of one mol of a monoatomic ideal gas when the temperature goes from 0°C to 50°C.
- ✓**21.39 Steam is used to cool a polymer reaction. The steam in the steam chest of the apparatus is found to be at 250.5°C and 4000 kPa absolute during a routine measurement at the beginning of the day. At the end of the day the measurement showed that the temperature was 650°C and the pressure 10,000 kPa absolute. What was the internal energy change of 1 kg of steam in the chest during the day? Obtain your data from the steam tables.
- *21.40 What is the difference between heat and internal energy?
- *21.41 Explain why, when a liquid evaporates, the change in enthalpy is greater than the change in internal energy
- *21.42 One pound of liquid water is at its boiling point of 575°F. It is then heated at constant pressure to 650°F, and then compressed at constant temperature to one-half of its volume (at 650°F), and finally returns to its original state of the boiling point at 575°F. Calculate ΔH and ΔU for the overall process.
- *21.43 A gas is heated at 200 kPa from 300 K to 400 K, and then cooled to 350 K. In a different process the gas is directly heated from 300 K to 350 K at 200 kPa. What difference is there in internal energy and enthalpy changes for the two processes?
- *21.44 For the systems defined below, state whether Q , W , ΔH , and ΔU are 0, > 0 , or < 0 , and compare their relative values if not equal to 0:
- An egg (the system) is placed into boiling water.
 - Gas (the system), initially at equilibrium with its surroundings, is compressed rapidly by a piston in an insulated nonconducting cylinder by an insulated nonconducting piston; give your answer for two cases: (1) before reaching a new equilibrium state, and (2) after reaching a new equilibrium state.
 - A Dewar flask of coffee (the system) is shaken.
- ✓***21.45 (a) Ten pound moles of an ideal gas are originally in a tank at 100 atm and 40°F. The gas is heated to 440°F. The specific molar enthalpy, \hat{H} , of the ideal gas is given by the equation

$$\hat{H} = 300 + 8.00T$$

where \hat{H} is in Btu/lb mol and T is the temperature in °F.

- Compute the volume of the container (ft³).
 - Compute the final pressure of the gas (atm).
 - Compute the enthalpy change of the gas.
- (b) Use the equation above to develop an equation giving the molar internal energy, \hat{U} , in J/g mol as a function of temperature, T , in °C.
- ✓***21.46 You have calculated that specific enthalpy of 1 kg mol of an ideal gas at 300 kN/m² and 100°C is 6.05×10^5 J/kg mol (with reference to 0°C and 100 kN/m²). What is the specific internal energy of the gas at 300 kPa and 100°C?
- *21.47 Answer the following questions true or false:
- In a process in which a pure substance starts at a specified temperature and pres-

sure, goes through several temperature and pressure changes, and then returns to the initial state, $\Delta U = 0$.

- (b) The reference enthalpy for the steam tables ($\Delta H = 0$) is at 25°C and 1 atm.
- (c) Work can always be calculated as $\Delta(pV)$ for a process going from state 1 to state 2.
- (d) An isothermal process is one for which the temperature change is zero.
- (e) An adiabatic process is one for which the pressure change is zero.
- (f) A closed system is one for which no reaction occurs.
- (g) An intensive property is a property of material that increases in value as the amount of material increases.
- (h) Heat is the amount of energy liberated by the reaction within a process.
- (i) Potential energy is the energy a system has relative to a reference plane.
- (j) The units of the heat capacity can be (cal)/(g)(°C) or Btu/(lb)(°F), and the numerical value of the heat capacity is the same in each system of units.

***21.48** Answer the following questions true or false:

- (a) The enthalpy change of a substance can never be negative.
- (b) The enthalpy of steam can never be less than zero.
- (c) Both Q and ΔH are state (point) functions.
- (d) Internal energy does not have an absolute value.
- (e) By definition $U = H - (pV)$.
- (f) The work done by a gas expanding into a vacuum is zero.
- (g) An intensive property is a property whose value depends on the amount of material present in the system.
- (h) The enthalpy change for a system can be calculated by just taking the difference between the final and initial values of the respective enthalpies.
- (i) Internal energy has a value of zero at absolute zero.
- (j) A batch system and an open system are equivalent terms.
- (k) $\left(\frac{\partial U}{\partial p}\right)_T = 0$ for an ideal gas.
- (l) Enthalpy is an intensive property.
- (m) Internal energy is an extensive property.
- (n) The value of the internal energy for liquid water is about the same as the value for the enthalpy.

CHAPTER 22

INTRODUCTION TO ENERGY BALANCES FOR PROCESSES WITHOUT REACTION

22.1 The Concept of the Conservation of Energy	646
22.2 Energy Balances for Closed, Unsteady-State Systems	648
22.3 Energy Balances for Closed, Steady-State Systems	655
22.4 Energy Balances for Open, Unsteady-State Systems	657
22.5 Energy Balances for Open, Steady-State Systems	666

Your objectives in studying this chapter are to be able to

1. Classify for a given problem the process as (a) an open or closed system and (b) a steady-state or unsteady-state system.
2. Write a correct energy balance for a selected system.
3. Simplify the general energy balance to eliminate as many unimportant terms as possible based on the process conditions.
4. Calculate values of temperature, pressure, heat, work, internal energy, and enthalpy by solving simplified energy balances.

So far you have studied the details of setting up and solving mass balances. An equally important and useful concept is that of energy balances. You will need both tools to solve problems in practice.

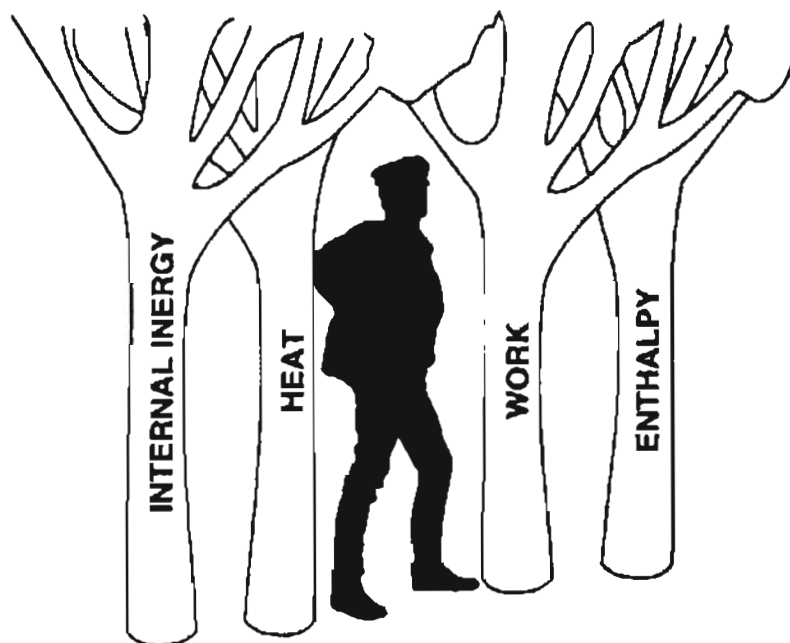


Figure 22.0 You're not out of the woods yet.

Looking Ahead

In Chapter 21 we discussed Q , W , U , and H , but did not try to relate them in an energy balance. In this chapter we explain what energy balances are all about. We also show you how to formulate, simplify, and solve energy balances for variables of interest. Our attention will be focused on techniques for the application to steady- and unsteady-state processes for both open and closed systems. Because this is an introductory chapter, only simple balances without chemical reaction will be involved. Chapter 24 covers more complex applications, and Chapters 25 and 26 covers balances in which chemical reactions occur in a process.

22.1 The Concept of the Conservation of Energy

As you know, the principle of the **conservation of energy** states that the total energy of the *system plus the surroundings* can neither be created nor destroyed.*

Die Energie der Welt ist Konstant.

Clausius

*Can mass be converted into energy according to $E = mc^2$? It is not correct to say that $E = mc^2$ means mass is converted into energy. The equal sign can mean that two quantities have the same value as in measurements of two masses in an experiment, or it may mean (as in general relativity) that the two variables are the same or are equivalent things. It is in the latter sense that $E = mc^2$ applies, and not in terms of converting a *rest mass* into energy. You might write $\Delta E = c^2 \Delta m$. If Δm is negative, ΔE is also negative. What this means is as the *inertia mass* decreases, ΔE decreases, and the reverse.

This principle is based on well founded experimental measurements. During an interaction between a system and its surroundings, the amount of energy gained by the system must be exactly equal to the amount of energy lost by the surroundings. Rather than focus on the words the “law of the conservation of energy” in this book, we will use the words “energy balance” to avoid confusion with the colloquial use of the words “energy conservation”, that is, reduction of energy waste or increased efficiency of energy utilization. Keep in mind four important points as you read what follows.

1. We examine only systems that are homogeneous, not charged, and without surface effects, in order to make the energy balance as simple as possible.
2. The energy balance is developed and applied from the macroscopic viewpoint (overall about the system) rather than from a microscopic viewpoint (i.e., an elemental volume within the system).
3. All the equations represent cumulative quantities over a time interval. Chapter 32 treats differential equations.
4. We defer consideration of the effect of chemical reactions until Chapter 25.

As America entered World War I in 1917, an Armenian named Garabed Giragossian petitioned Congress to investigate his miraculous and eponymous Garabed, an invention that would provide unlimited energy, “a natural force that we can utilize and have energy as we like, without toil or expense.” First he secured the endorsements of the Director of Music in the Boston Public Schools, the President of the Board of Trustees of the Boston Public Library, and the President of a shipbuilding concern; when he began his lobbying campaign on Capital Hill, reports about his machine appeared in *The Literary Digest* and the *St. Louis Post-Dispatch*. The house voted 234 to 14 to investigate the Garabed. The congressional investigation revealed that Giragossian had made the most elementary of errors; he had confused power and force. The Garabed was a simple flywheel set spinning manually with pulleys and kept in motion with an electric motor. Giragossian hoped to extract his “free energy” from the difference between the 10 horsepower required to stop the wheel and the 20th of one horsepower needed to keep it going; he failed to realize that when the wheel was stopped quickly, it spent all of the energy it had gradually stored up.

In more recent times inventors have been able to demonstrate devices that indeed put out more energy than was put in. Most of such devices have been based on charging and discharging a storage battery repeatedly. Each time more electrical energy is recovered than used to charge the battery (as long as it is not charged too rapidly). How is this outcome possible? If you do not know, look at the footnote on the next page.

We will start our trip with closed systems and then proceed to open systems. Learn how to recognize the character of the process involved, and what suitable approximations and simplifications can be made in the energy balances.

SELF-ASSESSMENT TEST

Questions

1. Does the principle of the conservation of energy state that energy cannot be created or destroyed?
2. Explain the difference in concept between the law of the conservation of energy and the statement of an energy balance.
3. Does the energy balance carry out an accounting of the molecular translational, rotational, and vibrational energy of materials?

Discussion Problems

1. Why is the term “energy conservation” misleading when used in connection with the practice of conserving our energy resources?
2. Transportation of people and goods currently consume about 25% of the total energy use in the United States. Everyone indicates that considerable energy could be saved if new and revised methods of transportation could be implemented. But how much? Examine various scenarios of change, and estimate the related reduction of energy use.

22.2 Energy Balances for Closed, Unsteady-State Systems

*Open your mind to what I shall explain,
then close around it, for it is no learning
to understand what one does not retain.*

—Canto V, 40–42

Do you recall that the essence of a closed system is one in which no mass goes in or out of the system? If so, what types of energy can be exchanged between a system and its surroundings? Only work and heat are allowed. Typical examples are batch processes, described in Chapter 7. Batch processes are used to manufacture specialized pharmaceuticals and polymer products usually in low production quantities. Unsteady state means that the state of the material inside the system changes. You know that for a closed, unsteady-state system the macroscopic mass balance for a given time interval in words is

The battery heats up and can deliver more watts at the higher temperatures.

$$\left\{ \begin{array}{l} \text{accumulation of} \\ \text{mass within the} \\ \text{system boundary} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} = \left\{ \begin{array}{l} \text{net transfer of mass into} \\ \text{the system through the} \\ \text{system boundary} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} - \left\{ \begin{array}{l} \text{net transfer of mass out} \\ \text{of the system through} \\ \text{the system boundary} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\}$$

and in symbols is

$$\Delta m_{\text{system}} = m_{\text{in}} - m_{\text{out}} \quad (22.1)$$

In this book, rates have overlay dots on m (\dot{m}), and specific (per unit mass) values will have overlay carets (\hat{m}) placed on m .

By analogy we can write the macroscopic **energy balances** for a closed, unsteady-state system for a given time interval in words as

$$\left\{ \begin{array}{l} \text{accumulation of} \\ \text{energy within} \\ \text{the system} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} = \left\{ \begin{array}{l} \text{net transfer of energy} \\ \text{into the system through} \\ \text{system boundary} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} - \left\{ \begin{array}{l} \text{net transfer of energy} \\ \text{out of the system through} \\ \text{system boundary} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\}$$

and replacing the words with the symbols we used in Chapter 21

$$\Delta (U + PE + KE)_{\text{inside}} \equiv \Delta E = Q + W \quad (22.2)$$

We do not put a Δ representing the final minus initial states symbol before Q or W because they are not state variables. Remember that Q and W are both *positive* when transferred into the system, and E represents the sum of $(U + KE + PE)$ associated with *mass in the system* itself, as shown in Figure 22.1. (Be careful; in some books W is defined as positive when done by the system.)

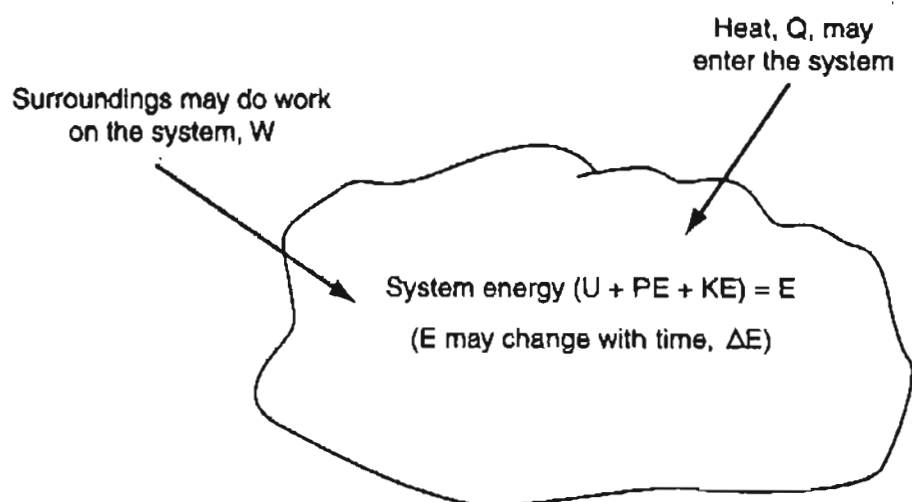


Figure 22.1 A closed, unsteady-state system with heat (Q) and work (W).

Also keep in mind that each term in Equation (22.2) represents the respective *net cumulative* amount of energy over the time interval from t_1 to t_2 , not the respective energy per unit time, a rate, which would be denoted by an overlay dot.

In closed systems, except for falling stones and cannon balls, the values of ΔPE and ΔKE in ΔE are usually negligible or zero, hence often you see $\Delta U = Q + W$ used as the energy balance. You will find that closed systems occur far less frequently than the open systems that we will discuss in Sections 22.4 and 22.5.

If the sum of Q and W is positive, ΔE increases; if negative, ΔE decreases. Can you say that $\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$? Of course. Does $W_{\text{system}} = -W_{\text{surroundings}}$? Not necessarily, as you will learn in Chapter 27. For example, in Figure 22.2c the electrical work done by the surroundings on the system degrades into heating of the system, not in expanding its boundaries. But you can say $(Q + W)_{\text{system}} = -(Q + W)_{\text{surroundings}}$.

Julius Mayer (1814–1878) gave the first precise quantitative formulation of the principle of the conservation of energy. A journal refused to publish his ideas originally and many of his contemporaries laughed at him when he explained his ideas. Ph. von Jolly said that if what Mayer proposed was true, it should be possible to heat water by shaking it! Which, of course, you can do if you experiment properly.

Figure 22.2 illustrates three examples of applying Equation (22.2) to closed, unsteady-state systems. In Figure 22.2a, 10 kJ of heat is transferred through the fixed boundary (bottom) of a vessel with 2 kJ being transferred out at the top during the same time period. Thus, ΔU increases by 8 kJ. In Figure 22.2b, a piston does 5 kJ of work on a gas whose internal energy increases by 5 kJ. In Figure 22.2c, the voltage difference between the system and surroundings forces a current into a system in which no heat transfer occurs because of the insulation on the system.

The next examples will help you to ascertain how good your grasp is of the concept of applying energy balances to closed, unsteady-state systems.

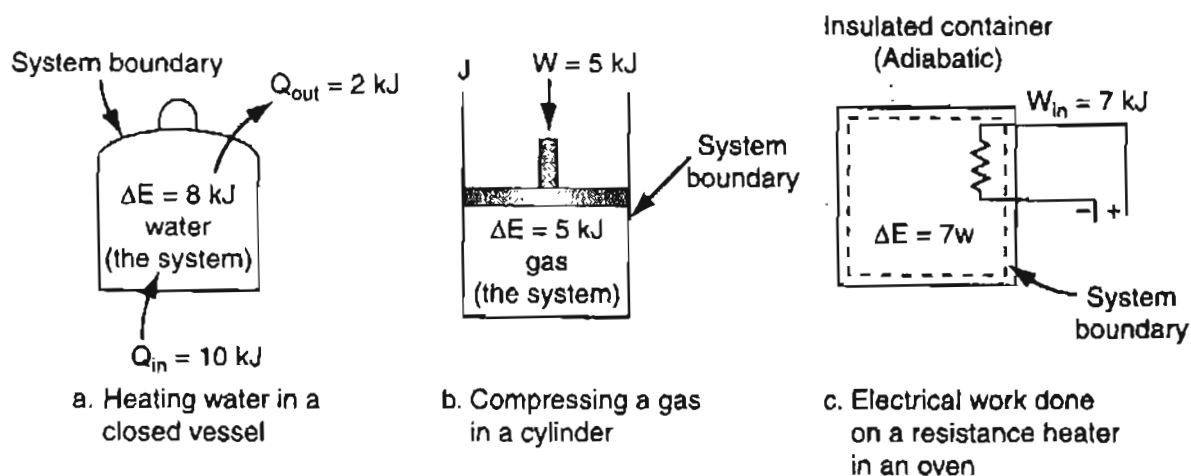


Figure 22.2 Examples of closed, unsteady-state systems that involve energy changes.

EXAMPLE 22.1 Application of the Energy Balance to a Closed System

Alkaloids are chemical compounds containing nitrogen that can be produced by plant cells. In an experiment, a closed vessel 1.673 m^3 in volume was filled with a dilute water solution containing two alkaloids, ajmalicine, and serpentine. The temperature of the solution was 10°C . To obtain an essentially dry residue of alkaloids, all of the water in the vessel (1 kg) was vaporized. Assume that the properties of water can be used as a substitute for the properties of the solution. How much heat has to be transferred to the vessel if 1 kg of saturated liquid water initially at 10°C is completely vaporized to the final conditions of 100°C and 1 atm ? See Figure E22.1.

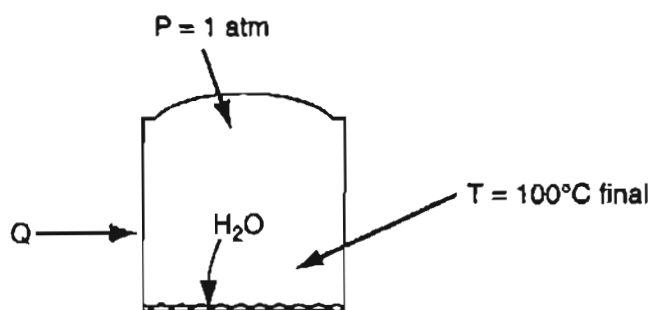


Figure E22.1

Solution

Sufficient data is given in the problem statement to fix the initial state and the final state of the water. You can look up the properties of water in the steam tables or on the CD in the back of this book. Note that the specific volume of steam at 100°C and 1 atm is $1.673 \text{ m}^3/\text{kg}$.

Initial state (liquid)		Final state (gas)
p	1 atm	1 atm
T	10.0°C	100°C
\hat{U}	35 kJ/kg	2506.0 kJ/kg

You can look up additional properties of water such as \hat{V} and \hat{H} , but they are not needed for the problem.

The system is closed, unsteady state so that Equation (22.2) applies

$$\Delta E = \Delta U + \Delta PE + \Delta KE = Q + W$$

Because the system (the water) is at rest, $\Delta KE = 0$. Because the center of mass of the water changes so very slightly, $\Delta PE = 0$. No work is involved (fixed tank boundary). You can conclude using a basis of

Basis: 1 kg H₂O evaporated

that

$$Q = \Delta U = m\Delta\hat{U} = m(\hat{U}_2 - \hat{U}_1)$$

$$Q = \frac{1 \text{ kg H}_2\text{O}}{\text{kg}} \left| \frac{(2506.0 - 35) \text{ kJ}}{\text{kg}} \right| = 2471 \text{ kJ}$$

Note that in Example 22.1 we used the SI system of units in the problem statement and solution. If the problem were posed in the AE system of units, as in the next example, and you use the steam tables, you will often find only enthalpy values listed (not the case with the steam tables in the foldout in the back of this book). Then you would have to calculate Q from

$$Q = \Delta U = \Delta H - \Delta(pV) \quad (22.3)$$

and will have to look up and use values of p and \hat{V} , a nuisance avoided by getting the steam properties from the CD in the back of this book.

EXAMPLE 22.2 Calculation of ΔU Using American Engineering Units

Saturated liquid water is cooled from 80°F to 40°F still saturated. What are $\Delta\hat{E}$, $\Delta\hat{U}$, $\Delta\hat{H}$, $\Delta\hat{p}$, and $\Delta\hat{V}$?

Solution

The system is closed and unsteady state, and thus analogous to Example 22.1. The properties listed below are from the steam tables for saturated liquid (at its vapor pressure).

	Initial Conditions	Final Conditions
p^* (psia)	0.5067	0.1217
\hat{V} (ft ³ /lb)	0.01607	0.01602
\hat{H} (Btu/lb)	48.02	8.05

Basis: 1 lb water

Then

$$\Delta\hat{p} = (0.1217 - 0.5067) = -0.385 \text{ psia}$$

$$\Delta\hat{V} = (0.01602 - 0.01607) = \text{negligible value}$$

$$\Delta\hat{H} = (8.05 - 48.02) = -39.97 \text{ Btu/lb}$$

$$\hat{W} = 0$$

$$\Delta \hat{KE} = 0$$

$$\Delta \hat{PE} = 0$$

Now $\Delta \hat{U} = \Delta \hat{H} - \Delta(p\hat{V})$

$$\Delta(p\hat{V}) = p_2\hat{V}_2 - p_1\hat{V}_1$$

$$= \frac{0.1217 \text{ lb}_f}{\text{in.}^2} \left| \frac{144 \text{ in.}^2}{1 \text{ ft}^2} \right| \frac{0.01602 \text{ ft}^3}{\text{lb}_m} \left| \frac{1 \text{ Btu}}{778(\text{ft})(\text{lb}_f)} \right|$$

$$- \frac{0.5067 \text{ lb}_f}{\text{in.}^2} \left| \frac{144 \text{ in.}^2}{1 \text{ ft}^2} \right| \frac{0.01607 \text{ ft}^3}{\text{lb}_m} \left| \frac{1 \text{ Btu}}{778(\text{ft})(\text{lb}_f)} \right|$$

$$= -1.141 \times 10^{-3} \text{ Btu} \quad \text{a negligible quantity}$$

Thus

$$\Delta \hat{U} = \Delta \hat{H} = -39.97 \text{ Btu/lb}$$

For a change in state of a liquid to a vapor, $\Delta(p\hat{V})$ may not be negligible.

SELF-ASSESSMENT TEST

Questions

1. Answer the following questions true or false:
 - a. The law of the conservation of energy says that all of the energy changes in a system must add up to zero.
 - b. The law of the conservation of energy says that no net change, or no creation or destruction of energy, is possible in a system.
 - c. The law of the conservation of energy says that any change in heat that is not exactly equal and opposite to a change in work must appear as a change in the total internal energy in a system.
 - d. Heat can flow into, and out of, a system to its surroundings. Work can be done by the system on the surroundings, and vice versa. The internal energy of a system can increase or decrease by any of these processes.
 - e. For all adiabatic processes between two specified states of a closed system, the net work done is the same regardless of the nature of the closed system and the details of the process.
 - f. A closed, unsteady-state system cannot be an isothermal system.
 - g. Heat transfer to an closed, unsteady-state system cannot be zero.
 - h. A closed system must be adiabatic.

2. Can heat be converted completely into work?
3. Look at Figure SAT22.2Q3

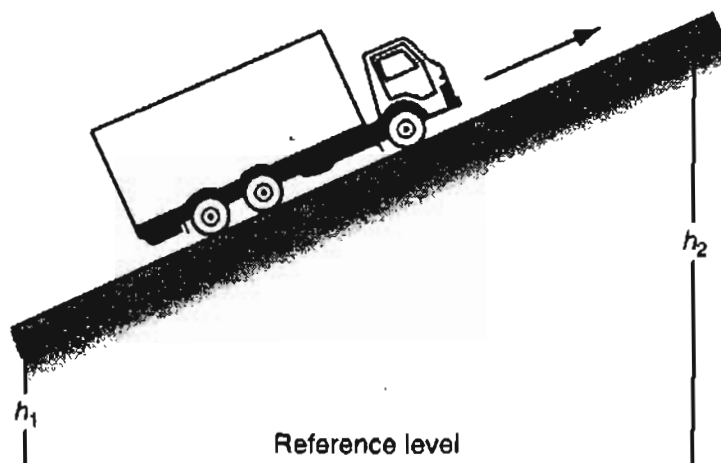


Figure SAT22.2Q3

- a. What system would you pick to calculate the power (work per unit time) required to transport the truck uphill?
- b. Would the system be open, closed, steady state, or unsteady state?
4. What does the symbol Δ stand for in the energy balance for a closed system?

Problems

1. A closed system undergoes three successive stages in which the respective heat transfers are: $Q_1 = +10$ kJ, $Q_2 = +30$ kJ, and $Q_3 = -5$ kJ, respectively. In the first stage, $\Delta E = +20$ kJ, and in the third stage, $\Delta E = -20$ kJ. What is the work in the second stage, and the net work output of all three stages?
2. A closed tank contains 20 lb of water. If 200 Btu are added to the water, what is the change in internal energy of the water?
3. When a batch of hot water at 140°F is suddenly well mixed with cold water at 50°F , the water that results is at 110°F . What was the ratio of the hot water to the cold water? You can use the steam tables to get the data.

Thought Problems

1. Does the Law of the Conservation of Energy explain how energy can be extracted from uranium in a nuclear reactor?
2. Does the Law of the Conservation of Energy state that energy can neither be created nor destroyed?
3. The current concern with "renewable" energy seems to be a paradox because of the Law of the Conservation of Energy. Wind mills extract power from the wind and convert it to electricity. Will this affect the weather in some way?

Discussion Problem

1. The head of a small electronics firm solicited money to develop a device that uses noise from an engine or other source to generate electricity. He said, "By using automobile noise the device could furnish enough power to handle the lights, air conditioning, radio, and so on, everything except the power to start the car." In what term in the energy balance would the noise be accommodated? Do you think that the device would be practical?

22.3 Energy Balances for Closed, Steady-State Systems

Recall that steady state means the accumulation in the system is zero, and that the flows of Q and W in and out of the system are constant. They can actually vary in the process, of course, but we are really interested only in their net cumulative values over a time interval, and look at only the final and initial conditions for ΔE .

How should Equation (22.2) be modified to analyze steady-state systems? All you have to do is realize that inside the system

$$\begin{aligned}\Delta KE &= 0 & \Delta U &= 0 \\ \Delta PE &= 0 & \Delta E &= 0\end{aligned}$$

$$\text{hence} \quad Q + W = 0 \quad (22.4)$$

If you rearrange Equation (22.4), you get $W = -Q$, meaning that all of the work done on a closed, steady-state system must be transferred out as heat ($-Q$). However, ironically, the reverse is false, namely the heat added to a *closed, steady-state system* Q does not always equal the work done by the system ($-W$). If this were true you could construct a perpetual motion machine by building a thermoelectric engine that would transfer heat from a system at high temperature, convert all of the heat to work, and convert the work back to heat at the high temperature in order to run the cycle once more. The second law of thermodynamics states the conditions that make it impossible to construct such a perpetual motion machine. You will learn about this topic when you study thermodynamics, or if you read one of the many references at the end of the chapter.

Furthermore, if $Q = -W$ for a closed, steady-state system, you can calculate Q from the work done on the system, but if W is unknown Q would have to be calculated from an empirical relation such as $Q = UA\Delta T$, as discussed in Chapter 21, and Q would not necessarily equal ($-W$).

Figure 22.3 illustrates some examples of closed, steady-state systems with energy interchange. Contrast them with the figures in Figure 22.2.

In the processes shown in Figure 22.3, you can calculate Q and W as follows:

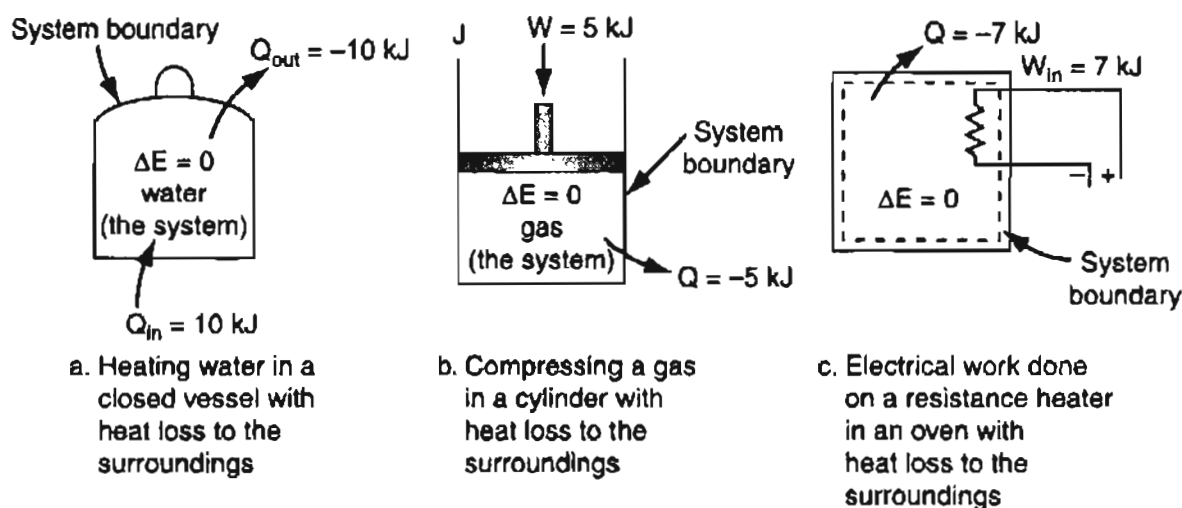


Figure 22.3 Examples of closed, steady-state systems that involve energy changes.

- Fig. a. $W = 0$ and hence $Q = 0$ (Q is the cumulative *net* heat transfer in Equation (22.4).)
- Fig. b. $W = 5 \text{ kJ}$ and hence $Q = -5 \text{ kJ}$
- Fig. c. $W = 7 \text{ kJ}$ and hence $Q = -7 \text{ kJ}$

In summary, for a closed, steady-state system, the energy balance reduces to Equation (22.4).

SELF-ASSESSMENT TEST

Questions

- Answer the following questions true or false.
 - The heat removed from a closed, steady-state system equals the work done on the system.
 - Volume is a conserved variable—in every case the change in the volume of a system is equal and opposite to the change in volume of the surroundings.
 - Any intensive property (such as T or p) cannot be subject to a conservation law as is energy.
- Does the transfer of heat into a closed, steady-state system increase or decrease the internal energy in the system?
- What are the assumptions made to reduce the general energy balance, Equation (22.2), to $Q = -W$?

Problems

- Examine Figure SAT22.3PI. What is ΔE ?

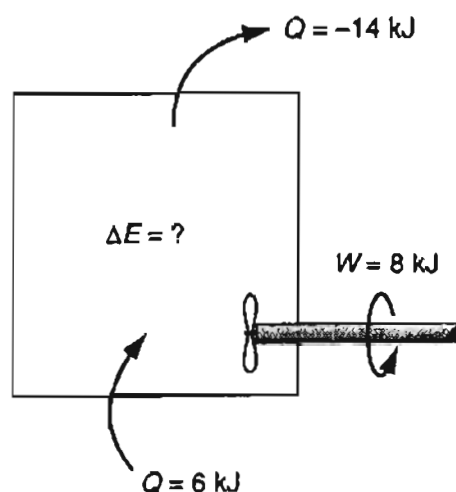


Figure SAT22.3P1

Discussion Problem

1. Is our planet an open or closed system with regard to the general energy balance? Discuss the various energy forms that are involved in the analysis.

22.4 Energy Balances for Open, Unsteady-State Systems

We shall not cease from exploration, and the end of all our exploring will be to arrive where we started and to know the place for the first time.

T.S. Eliot

Now that we have discussed closed systems, it is time to focus on processes represented by open systems, the occurrence of which is much more common than closed systems.

In an open, unsteady-state system, the accumulation term (ΔE) in the energy balance can be nonzero because

1. the mass in the system changes,
2. the energy per unit mass in the system changes, and
3. both 1 and 2 occur.

You know that when mass flows in and out of a system the mass carries energy along with it. What types of energy? Just the same types that are associated with the mass inside the system, namely U , PE , and KE . All you have to do, then, is add these three types of energy associated with each stream going in and out of the system to the energy transfers of Q and W in the energy balance, Equation (22.2), to

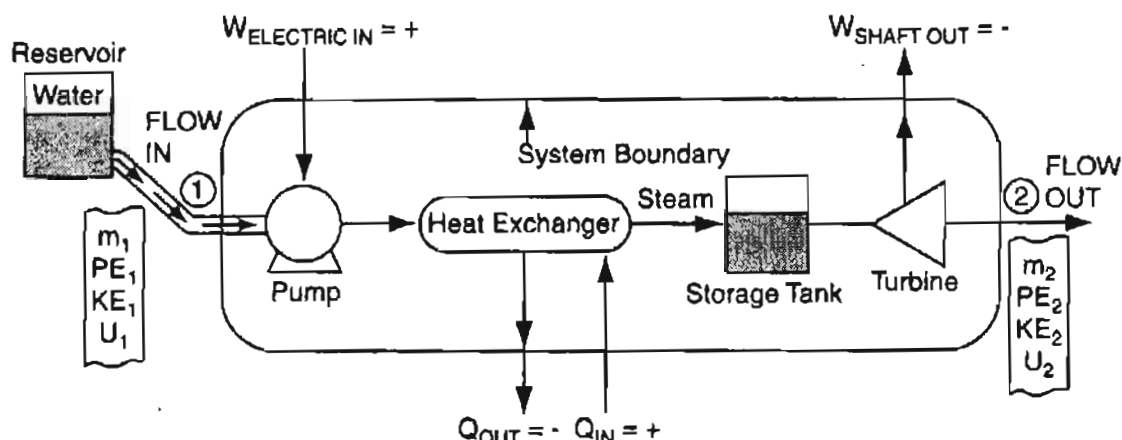


Figure 22.4 An open, unsteady-state system. The system is inside the boundary. (1) and (2) denote sections for entering and exiting mass flows, respectively. The liquid level and mass in the storage tank, and possibly the temperature, can vary.

make a **general energy balance** that is valid for both open systems and closed systems without reaction. ΔE will still correspond the *final state within the system minus the initial state within the system*.

Figure 22.4 illustrates a general open system with one stream entering and one leaving. We are not concerned with the details of the process—only with the energy transfers into and out of the system, and changes within the system as a whole. Table 22.1 lists the notation that we will use in formulating the general energy balance. The overlay caret (^) still means the energy term per unit mass, and m with the subscript t_1 or t_2 denotes mass at time t_1 or t_2 , respectively, whereas m with the subscript 1 or 2 denotes the total flow of mass between t_1 and t_2 at section 1 or 2, respectively, in Figure 22.4.

Note that in Table 22.1 we have split the work term into parts, as mentioned in Chapter 21.

For a specified time interval, you can assemble each of the terms that will be in the general energy balance using the symbols given in Table 22.1 as follows:

Accumulation in the system from t_1 to t_2 :

$$\Delta E \equiv m_{t_2} (\hat{U} + \hat{KE} + \hat{PE})_{t_2} - m_{t_1} (\hat{U} + \hat{KE} + \hat{PE})_{t_1}$$

Energy transfer in with mass from t_1 to t_2 : $(\hat{U}_1 + \hat{KE}_1 + \hat{PE}_1)m_1$

Energy transfer out with mass from t_1 to t_2 : $(\hat{U}_2 + \hat{KE}_2 + \hat{PE}_2)m_2$

Net energy transfer by heat transfer in and out from t_1 to t_2 : Q

Net energy transfer by shaft, mechanical, or electrical work in and out from t_1 to t_2 : W

Net energy transfer by work to introduce and remove mass from t_1 to t_2 :

$$p_1 \hat{V}_1 m_1 - p_2 \hat{V}_2 m_2$$

TABLE 22.1 Summary of the Symbols to be Used in the General Energy Balances

Accumulation term (inside the system)		
Type of energy in the system	At time t_1	At time t_2
Internal	U_{t_1}	U_{t_2}
Kinetic	KE_{t_1}	KE_{t_2}
Potential	PE_{t_1}	PE_{t_2}
Mass of the system	m_{t_1}	m_{t_2}
Energy accompanying mass transport (through the system boundary) during the time interval t_1 to t_2		
Type of energy	Transport in	Transport out
Internal	U_1	U_2
Kinetic	KE_1	KE_2
Potential	PE_1	PE_2
Mass of the flow	m_1	m_2
Net heat exchange between the system and the surroundings during the interval t_1 to t_2		
		Q
Work terms (exchange with the surroundings) during the interval t_1 to t_2		
Net shaft, mechanical, and electrical work		$W \begin{cases} W_{\text{shaft}} \\ W_{\text{mechanical}} \\ W_{\text{electrical}} \end{cases}$
Flow work done on the system to introduce material into the system	$m_1(p_1\hat{V}_1)$	
Flow work done on the surroundings to remove material from the system		$-m_2(p_2\hat{V}_2)$

The quantities $p_1\hat{V}_1$ and $p_2\hat{V}_2$ probably need a little explanation. They represent the so-called “ pV work,” “pressure energy,” “flow work,” or “flow energy,” that is, the work done by the surroundings to put a mass of matter into the system at boundary 1 in Figure 22.4, and the work done by the system on the surroundings as a unit mass leaves the system at boundary 2, respectively. Because the pressures at the entrance and exit to the system are deemed to be constant for differential displacements of mass, the work done per unit mass by the surroundings on the system adds energy to the system at boundary 1:

$$\hat{W}_1 = \int_0^{\hat{V}_1} p_1 d\hat{V} = p_1(\hat{V}_1 - 0) = p_1\hat{V}_1$$

where \hat{V} is the volume per unit mass. Similarly, the work done by the fluid on the surroundings as the fluid leaves the system is $W_2 = -p_2\hat{V}_2$.

If we now combine all of the terms listed above into an energy balance, we get a somewhat formidable equation

$$\Delta E = (\hat{U}_1 + \widehat{KE}_1 + \widehat{PE}_1)m_1 - (\hat{U}_2 + \widehat{KE}_2 + \widehat{PE}_2)m_2 + Q + W + p_1\hat{V}_1m_1 - p_2\hat{V}_2m_2 \quad (22.5)$$

In formulating Equation (22.5), for simplicity we have assumed that the physical properties \hat{U} , \hat{H} , \widehat{KE} , \widehat{PE} , p , and \hat{V} associated with the mass flows are constant during the time interval for which the equation applies. The mass entering and leaving the system may vary with time, but the symbols m_1 and m_2 represent the total accumulation of mass entering and leaving the system, respectively, during the time interval. The heat transfer and work terms respectively represent the *net* of each of the energy transfers during the time interval t_1 to t_2 .

To simplify the notation in Equation (22.5), let us add

$$p_1\hat{V}_1m_1 \text{ to } \hat{U}_1m_1 \quad \text{and} \quad p_2\hat{V}_2m_2 \text{ to } \hat{U}_2m_2$$

to get

$$\Delta E = [(\hat{U}_1 + p_1\hat{V}_1) + \widehat{KE}_1 + \widehat{PE}_1]m_1 - [(\hat{U}_2 + p_2\hat{V}_2) + \widehat{KE}_2 + \widehat{PE}_2]m_2 + Q + W \quad (22.5a)$$

Next, introduce \hat{H} via the expression $\hat{U} + p\hat{V} = \hat{H}$ into Equation (22.5a) to get

$$\Delta E = (\hat{H}_1 + \widehat{KE}_1 + \widehat{PE}_1)m_1 - (\hat{H}_2 + \widehat{KE}_2 + \widehat{PE}_2)m_2 + Q + W \quad (22.5b)$$

You can now see why the variable called enthalpy appears in the general energy balance.

Because Equation (22.5b) is so long, we have a suggestion. To help you memorize the energy balance, change the notation a bit to what is used in many texts:

$$\Delta E = E_{t_2} - E_{t_1} = Q + W - \Delta(H + KE + PE) \quad (22.6)$$

where

$$E_t = (U + KE + PE)_t \text{ refers to inside the system at time } t$$

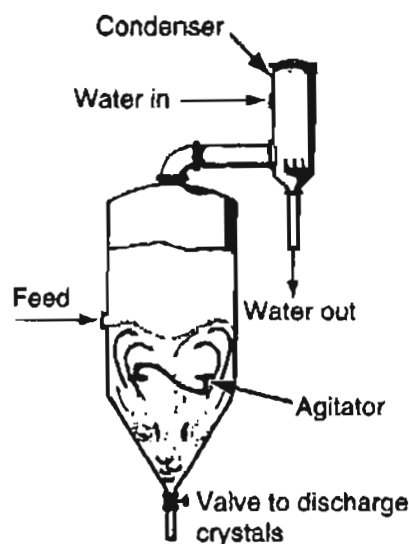
In Equation (22.6) the delta symbol (Δ) **standing for a difference** then has two different meanings.

- a. In ΔE , Δ means final minus initial in *time*.
- b. In $\Delta(H + PE + KE)$, Δ means *out of the system minus into the system*.

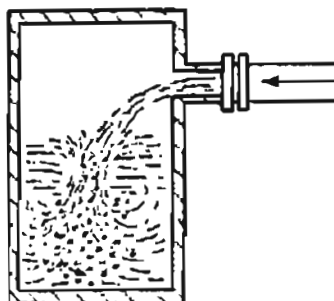
If you use Equation (22.6), be sure to link in your mind the two meanings of the Δ s to the respective terms in Equation (22.5b) to avoid any confusion.

To what kinds of processes can you apply the above equations? Look at Figure 22.5 for some examples. In Figure 22.5a, a feed comprised of salt in solution is sep-

a. Crystalizer (the crystals accumulate in the holding cone)



b. Filling a fixed volume tank with water



c. Batch distillation (distillation without replacement of feed)

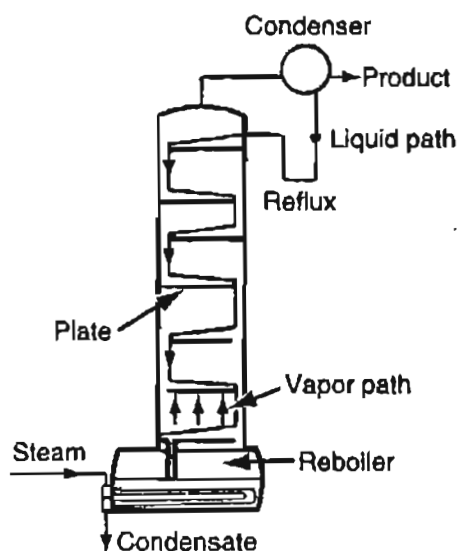


Figure 22.5 Examples of open, unsteady-state systems.

arated by crystallization. A vacuum is created in the condenser by very cold water to remove water vapor from above the liquid solution so as to concentrate it. Crystals that form are periodically discharged from the bottom of the crystallizer. In Figure 22.5b water discharges into and fills up a tank. In Figure 22.5c, two liquids are sepa-

rated by batch distillation. The distillation column is filled with the liquid to be separated; steam in the heat exchanger in the reboiler causes vapor to rise in the column that is of higher concentration in one component than the others, and can be condensed.

EXAMPLE 22.3 Use of the General Energy Balance to Analyze an Open, Unsteady-State System

A rigid, well-insulated tank is connected to two valves. One valve goes to a steam line that has steam at 1000 kPa and 600K, and the other to a vacuum pump. Both valves are initially closed. Then the valve to the vacuum pump is opened, the tank is evacuated, and the valve closed. Next the valve to the steam line is opened so that the steam enters the evacuated tank very slowly until the pressure in the tank equals the pressure in the steam line. Calculate the final temperature of the steam in the tank.

Solution

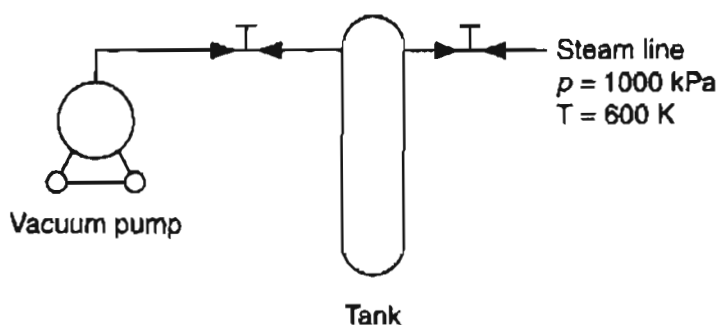


Figure E22.3a shows the process.

First, pick the tank as the system. If you do, the system is unsteady state (the mass increases in the system) and open. Pick a basis of 1 kg.

Next, get the data for steam at 1000 kPa and 600 K from the database in the CD in the back of this book:

$$\hat{U} = 2837.73 \text{ kJ/kg}$$

$$\hat{H} = 3109.44 \text{ kJ/kg}$$

$$\hat{V} = 0.271 \text{ m}^3/\text{kg}$$

Next, write down the general energy balance, Equation (22.6).

$$E_{t_2} - E_{t_1} = Q + W - \Delta(H + KE + PE) \quad (a)$$

and begin simplifying it. You can make the following assumptions:

1. No change occurs within the system for the PE and KE , hence $\Delta E = \Delta U$.
2. No work is done on or by the system because the tank is rigid; hence $W = 0$.
3. No heat is transferred to or from the system because it is well insulated, hence $Q = 0$.
4. The ΔKE and ΔPE of the steam entering the system are zero.
5. No stream exits the system, hence $H_{out} = 0$.
6. Initially no mass exists in the system, hence $U_{i1} = 0$.

Consequently Equation (a) reduces to

$$U_{t2} - 0 = -(H_{out} - H_{in})$$

$$\text{or} \quad \Delta U = U_{t2} = m_{in} \hat{U}_{t2} = -H_{in} = -m_{in} \hat{H}_{in} \quad (b)$$

To fix the final temperature of the steam in the tank, you have to determine two properties of the steam in the tank—any two. One value is given: $p = 1000$ kPa. What other property is known? Not T nor \hat{V} . But you can use Equation (b) to calculate \hat{U}_{t2} because

$$\hat{U}_{t2} = \hat{H}_{in} = 3109.44 \text{ kJ/kg} \quad (c)$$

and find from interpolating in the steam tables at $p = 1000$ kPa that $T = 764$ K.

You may wonder what the source of the energy is that causes the increase in temperature of the steam in the system over that in the steam line. Let us look at the problem via a closed system, namely a system consisting of (a) the volume of all of the steam in the steam line that eventually will be in the tank, plus (b) the volume of the tank itself. Examine Figure E22.3b.

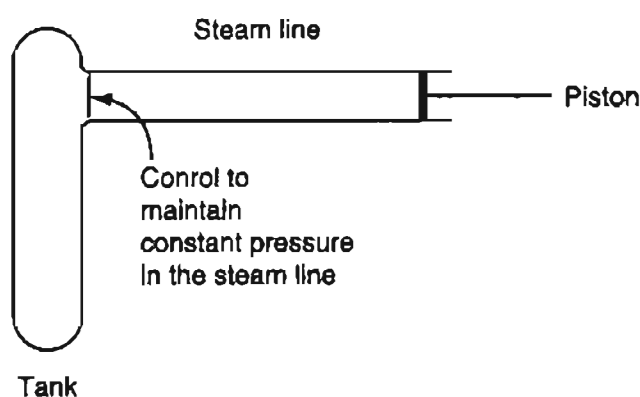


Figure E22.3b

Assume that a hypothetical piston very slowly compresses the volume of steam into the tank. The system boundary changes position during the compression so that the piston does work on the system.

A new assumption has to be made and a previous one changed.

1. No flow occurs into the system—it is closed—so $\hat{H}_{in} = 0$ in Equation (a).
2. Work is not zero but is done on the system at the constant pressure in the steam line (this might be hard to do in practice but is our assumption).
Then

$$\hat{W}_{in} = - \int_{\hat{V}_{t_1}}^{\hat{V}_{t_2}} p d\hat{V} = -p(\hat{V}_{t_2} - \hat{V}_{t_1}) \quad (d)$$

where \hat{V}_{t_2} is the volume of the tank, and \hat{V}_{t_1} is the volume of the tank plus the volume occupied by the steam in the system before it enters the tank. Do you see that $(\hat{V}_{t_2} - \hat{V}_{t_1})$ is just the negative of the volume of the steam in the system in the steam line? Thus

$$\hat{W}_{in} = p\hat{V}_{\text{steam line}} \quad (e)$$

and from Equation (a) with the new assumptions

$$\hat{U}_{t_2} = \hat{U}_{t_1} = \hat{W}_{in} = p\hat{V}_{\text{steam line}}$$

Now

$$\hat{U}_{t_1} = \hat{U}_{t_1 \text{ in tank}} + \hat{U}_{t_1 \text{ in line}} = \hat{U}_{in}$$

since

$$\hat{U}_{t_1 \text{ in tank}} = 0$$

Thus per kg

$$\hat{U}_{t_2} = \hat{U}_{in} + p\hat{V}_{in} = \hat{H}_{in} \quad (f)$$

as in Equation (b).

If there is more than *one input and output stream* for the system, you will find it becomes convenient to calculate the properties of each stream separately and sum the respective inputs and outputs so that Equation (22.5b) becomes the **general energy balance** (without reaction occurring)

$$\begin{aligned} \Delta E = E_{t_2} - E_{t_1} = & \sum_{\substack{\text{input} \\ \text{streams} \\ i=1}}^M m_i(\hat{H}_i + \widehat{KE}_i + \widehat{PE}_i) \\ & - \sum_{\substack{\text{output} \\ \text{streams} \\ o=1}}^N m_o(\hat{H}_o + \widehat{KE}_o + \widehat{PE}_o) + Q + W \end{aligned} \quad (22.7)$$

where $E_i = U_i + KE_i + PE_i$ inside the system

M = number of input streams

N = number of output streams

i = input stream

o = output stream

Each stream, of course, may contain more than one component so that the properties of a stream will be the sum of the properties of all of the components (plus any effect of mixing, which is discussed in Chapter 28). Equation (22.7) applies to open and closed systems as well as unsteady-state and steady-state systems.

SELF-ASSESSMENT TEST

Questions

1. Do turbines and pumps represent examples of unsteady-state systems?
2. Can a system with no moving parts be treated as an open, unsteady-state system?
3. Answer the following questions true or false:
 - a. The input stream to a process possesses kinetic energy.
 - b. The input stream to a process possesses potential energy.
 - c. The input stream to a process possesses internal energy.
 - d. The exit stream from the system does flow work.
 - e. The shaft work done by a turbine that is rotated by a fluid in a system is positive.
4. What assumptions must be made to reduce the general energy balance, Equation (22.6), to $Q = \Delta H$?
5. You read in an engineering book that

$$U_2 - U_1 = Q + W_{\text{nonflow}}$$

If you cannot find the notation list in the book, would you agree that the equation represents the energy balance for an open, unsteady-state system?

6. If you read in the same book that

$$U_2 - U_1 = Q + W_{\text{flow}} + g(h_2 - h_1)$$

would you agree that the equation represents an open, unsteady-state system?

7. Does the equation $Q = \Delta H$ apply to open, unsteady-state processes?
8. For an open, unsteady-state system, does the boundary of the system have to be fixed?

Problems

1. Simplify the general energy balance, Equation (22.6), as much as possible for each of the following circumstances (state which terms can be deleted and why):

- a. The system has no moving parts.
 - b. The temperature of the system and surroundings is the same.
 - c. The velocity of the fluid flowing into the system equals the velocity of the fluid leaving the system.
 - d. The fluid exits the system with sufficient velocity so that it can shoot out 3 meters.
2. Under what circumstances is $\Delta U = \Delta H$ for an open, unsteady-state system?
 3. A tank at a service station containing air at 100 kPa and 300 K is filled with air from a compressor that discharges air at 300 kPa and 400 K into the tank. After 1 kg of air is pumped into the tank, the pressure in the tank reaches 300 kPa and 400 K. How much heat was added to or removed from the tank during the filling?

Data for the air:

	\hat{H} (kJ/kg)	\hat{U} (kJ/kg)	\hat{V} (m ³ /kg)
100 kPa and 300 K	459.85	337.75	0.8497
300 kPa and 400 K	560.51	445.61	0.3830

Thought Problems

1. The valve on a rigid insulated cylinder containing air at a high pressure is opened briefly to use some of the air. Will the temperature of the air in the cylinder change? If so, how?
2. If you open the valve on an insulated tank that is initially evacuated, and let the atmospheric air enter until atmospheric pressure is reached, will the temperature of the air in the tank be higher, the same, or lower than the temperature of the atmosphere? Explain your answer.

Discussion Problems

1. Under what conditions can an unsteady-state flow process be solved as a closed, unsteady-state process?
2. In Kurt Vonnegut's famous novel *Cat's Cradle*, a form of ice is discovered that is more stable than normal ice, and contact with normal water eventually converts all of the normal water to a solid at room temperature with the predictable consequences for the existence of life. Can this outcome be analyzed using the general energy balance?

22.5 Energy Balance for Open, Steady-State Systems

As we mentioned earlier, you will find that the preponderance of industrial processes operate under continuous, steady-state conditions. Most processes in the refining and chemical industries are open, steady-state systems. You will find that continuous processes are most cost effective in producing high-volume products.

Because steady state means that all of the state properties (T , p , etc.) and the mass within the system are invariant with respect to time, the final and initial states

of the system are the same, and $\Delta E = 0$. Continuous means the flows of heat and mass into and out of the system are constant (even though they are not, they often can be hypothetically assumed to be some average flows). Consequently, Equation (22.6) becomes with $\Delta E = 0$

$$Q + W = \Delta(H + PE + KE) \quad (22.8)$$

When are ΔPE and ΔKE negligible? Because the energy terms in the energy balance in most open processes are dominated by Q , W , and ΔH , ΔPE , and ΔKE only infrequently need to be used in Equation (22.8). For example, consider the righthand side of Equation (22.8). An enthalpy change of 1000 J/kg is really quite small, corresponding in air to a temperature change of about 1 K. For the other terms on the righthand side of Equation (22.8) to be equivalent to 1000 J:

1. The PE change would require 1 kg to go up a distance of 100 m.
2. The KE change would require a velocity change from 0 to 45 m/s.

As a result, the equation most commonly applied to open, steady-state processes does not include any potential and kinetic energy changes

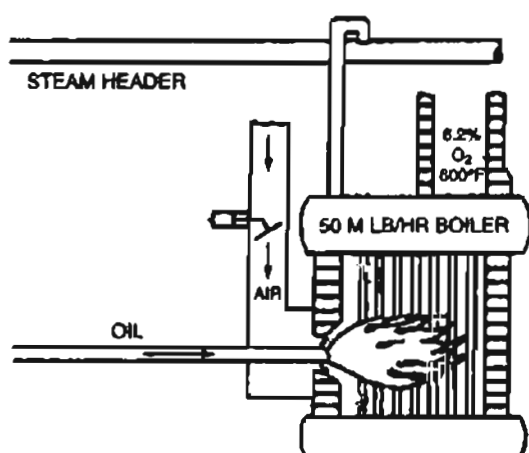
$$Q + W = \Delta H \quad (22.9)$$

Do not confuse Equation (22.9) with Equation (22.2), when $\Delta KE = \Delta PE = 0$ and you assume $\Delta E = \Delta U$ and $\Delta U \approx \Delta H$. Although the two equations then appear to be the same, the Δ in Equation (22.2) refers to a time difference, and in Equation (22.9) to a difference between flows in and out, and although superficially the equations appear to be the same, they actually refer to quite different processes.

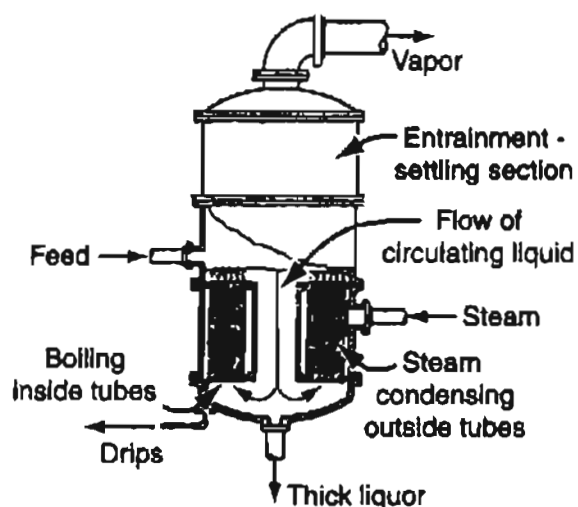
Figure 22.6 shows some examples of open, steady-state processes, and you will find more information about such processes in the CD that accompanies this book.

In Figure 22.6a, a fuel is burned in a boiler to heat tubes through which water flows and becomes steam. In Figure 22.6b, a dilute liquid feed containing a solute is concentrated to a "thick liquor." Vapor from the liquid is removed overhead. To provide the necessary heat, steam flows through a steam chest (heat exchanger). In Figure 22.6c, a liquid containing a desirable solute is passed through a column counter-current to an immiscible solvent that favors extracting the solute from the liquid. In Figure 22.6d, gas at high pressure flows over turbine blades, causing the shaft to rotate and do work. Finally, in the heat exchanger in Figure 22.6e, heat is transferred from the hot fluid flowing in the tubes to a cooler fluid that is being heated flowing across the tubes.

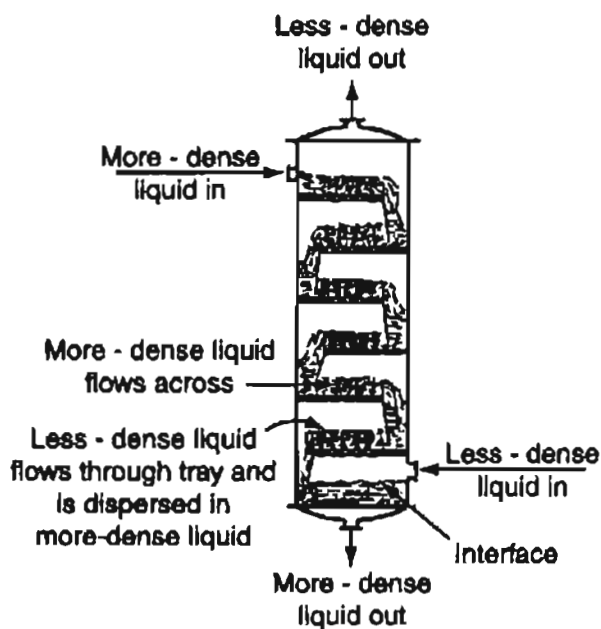
Now let's look at some problems and their solutions using Equations (22.8) and (22.9).



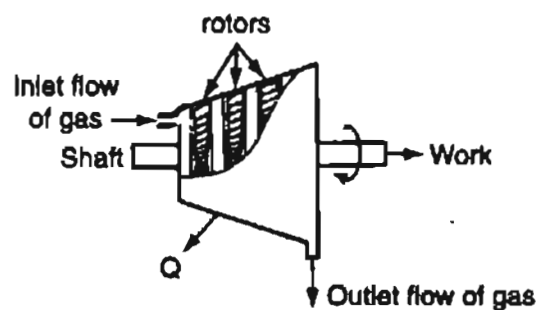
a. Boiler to generate steam



b. Evaporator that concentrates a solute



c. Plate extraction column



d. Turbine

Figure 22.6 Examples of open, steady-state processes.

Example 22.4 Application of the Energy Balance to a Open, Steady-State System, a Heat Exchanger

Milk (essentially water) is heated from 15°C to 25°C by hot water that goes from 70°C to 35°C, as shown in Figure E22.4. What assumptions can you make to simplify Equation (22.8), and what is the rate of water flow in kg/min per kg/min of milk?

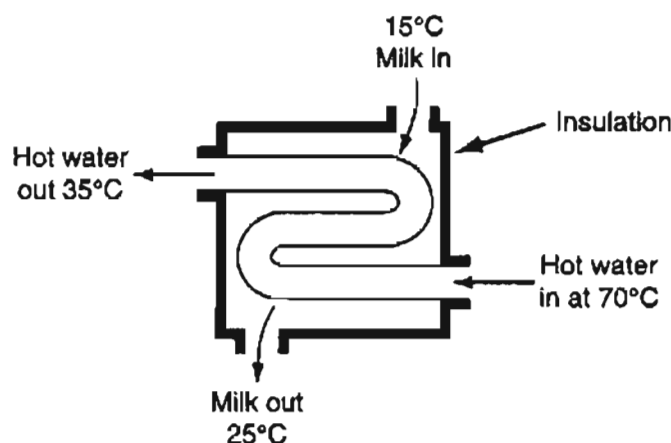


Figure E22.4

Solution

Pick the milk plus the water in the tank as the system. You could pick the milk (or the water) as the system so that heat is transferred from the water to the milk (the two fluids do not mix), but combining the two fluids as the system makes the analysis simple. What assumptions can be made to simplify Equation (22.8)? Here they are:

1. Certainly ΔKE and ΔPE are zero.
2. $Q = 0$ because of the way we picked the system—it is insulated.
3. $W = 0$.

With these assumptions Equation (22.8) becomes

$$\Delta H = 0 ! \quad (a)$$

Next, we collect the properties of water from the software database on the CD that accompanies this book or from the steam tables. Assume that the water is saturated, and that the milk has the same properties as water.

$T(^{\circ}\text{C})$	$\Delta \hat{H}(\text{kJ/kg})$
15	62.01
25	103.86
35	146.69
70	293.10

Let the basis be 1 min (the same as 1 kg of milk).

$$\frac{H_{\text{out}}}{[(1)\hat{H}_{\text{milk}, 25^\circ\text{C}} + (m)\hat{H}_{\text{water}, 35^\circ\text{C}}]} - \frac{H_{\text{In}}}{[(1)\hat{H}_{\text{milk}, 15^\circ\text{C}} + (m)\hat{H}_{\text{water}, 70^\circ\text{C}}]} = 0 \quad (\text{b})$$

$$[103.86 + (m)146.69] - [62.01 + (m)293.10] = 0$$

$$m = \frac{41.85}{146.41} = (0.29 \text{ kg hot water/min})/(\text{kg milk/min})$$

Let's repeat the problem solution but this time pick the milk as the system. The surroundings are comprised of the water and the tank. Now the assumptions to make in connection with using Equation (22.8) are:

1. $\Delta KE = \Delta PE = 0$
2. $W = 0$

Then Equation (22.8) reduces to

$$Q_{\text{water} \rightarrow \text{milk}} = \Delta H_{\text{milk}} = (1 \text{ kg})(\Delta \hat{H}_{\text{milk}} \text{ kJ/kg}) \quad (\text{c})$$

We know ΔH of the milk. What is Q ? Q has to be calculated from the properties of the water. Equation (22.8) gives for the water

$$-Q_{\text{water} \rightarrow \text{milk}} = (m \text{ kg})(\Delta \hat{H}_{\text{water}} \text{ kJ/kg}) \quad (\text{d})$$

The minus sign appears before Q because the heat transfer is out of the water into the milk.

If you combine Equations (c) and (d), you get

$$(1)\Delta H_{\text{milk}} - (m)\Delta \hat{H}_{\text{water}} = 0 \quad (\text{e})$$

or

$$((1)\hat{H}_{\text{milk}, 25^\circ\text{C}} - (1)\hat{H}_{\text{milk}, 15^\circ\text{C}}) - (m\Delta \hat{H}_{\text{water}, 70^\circ\text{C}} - m\Delta \hat{H}_{\text{water}, 35^\circ\text{C}}) = 0 \quad (\text{f})$$

Rearrange Equation (f) to get

$$(1)(\Delta \hat{H}_{\text{milk}, 25^\circ\text{C}} + m\Delta \hat{H}_{\text{water}, 35^\circ\text{C}}) - (\Delta \hat{H}_{\text{milk}, 15^\circ\text{C}} + m\Delta \hat{H}_{\text{water}, 70^\circ\text{C}}) = 0 \quad (\text{g})$$

Equation (g) is exactly the same as Equation (b), as you might anticipate. Just a different perspective was used in picking the system for analysis.

EXAMPLE 22.5 Calculation of the Power Needed to Pump Water in an Open, Steady-State System

Water is pumped from a well (Figure E22.5) in which the water level is a constant 20 feet below the ground level. The water is discharged into a level pipe that is 5 feet above the ground at a rate of 0.50 ft³/s. Assume that negligible heat transfer occurs from the water during its flow. Calculate the electric power required by the pump if it is 100% efficient and you can neglect friction in the pipe and the pump.

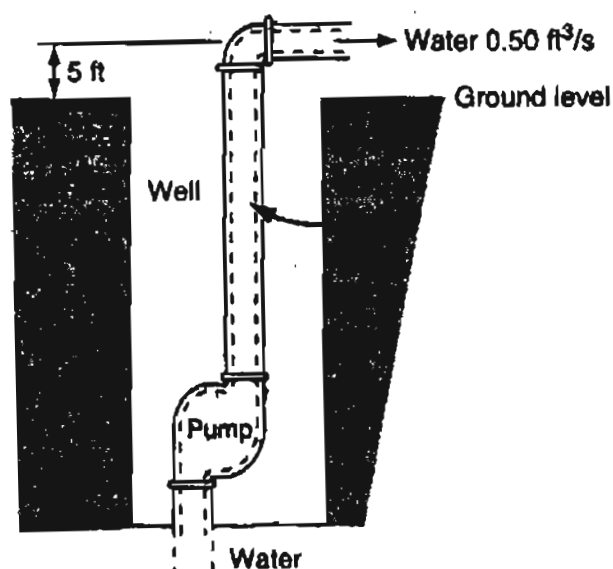


Figure E22.5

Solution

We will pick as the system the pipe from the water level in the well to the place where the water that exits is at 5 feet above the ground including the pump. Some assumptions that will help in simplifying Equation (22.8) are:

1. $Q = 0$ (given assumption)
2. $\Delta KE \approx 0$ (negligible change in KE ; you can verify this statement if you have doubts—assume a linear velocity at the top of the pipe equal to 7 ft/s, which is a typical value found in industrial applications).

What about ΔH ? Let us assume that the temperature of the water in the well is the same as the temperature of the water as it is discharged—a good assumption. Then Equation (22.8) reduces to

$$W = \Delta PE = mg(h_{\text{out}} - h_{\text{in}}) \quad (\text{a})$$

Choose a basis of 1 second. The mass flow is (say at 50°F)

$$\frac{0.50 \text{ ft}^3}{\text{s}} \left| \frac{62.4 \text{ lb}_m}{\text{ft}^3} \right| = 31.3 \text{ lb}_m \text{ water/s}$$

$$W = PE_{\text{out}} - PE_{\text{in}} = \frac{31.3 \text{ lb}_m \text{ H}_2\text{O}}{\text{s}} \left| \frac{32.2 \text{ ft}}{\text{s}^2} \right| \left| \frac{25 \text{ ft}}{32.2 \text{ (ft)(lb}_m\text{)}} \right| \left| \frac{(\text{s}^2)(\text{lb}_f)}{778.2 (\text{lb}_f)(\text{ft})} \right| \left| \frac{1.055 (\text{kW})(\text{s}^2)}{1} \right|$$

$$= 1.06 \text{ kW (1.42 hp)}$$

In Chapter 27 we discuss how to account for friction and pressure drop losses caused by pipe fittings and constrictions.

SELF-ASSESSMENT TEST

Questions

- Answer the following questions true or false:
 - The shaft work done by a pump and motor located inside the system is positive.
 - The Δ symbol in an energy balance for a steady-state system refers to the property of the material entering the system minus the property of the material leaving the system.
 - An input stream to a system does flow work on the system.
 - The input stream to a system possesses internal energy.
 - Work done by a fluid flowing in a system that drives a turbine coupled with an electric generator is known as flow work.
- What are two circumstances in which you can neglect the heat transfer term in the general energy balance?
- What term in the general energy balance is always zero for a steady-state process?
- What intensive variables are usually used to specify the value of the enthalpy?
- Under what condition can (a) the KE term, and (b) the PE term, be ignored or deleted from the general energy balance.

PROBLEMS

- A boiler converts liquid water to steam by letting the water flow through tubes that are heated by hot gases or another liquid. The pressure and flow rate of the water through the tubes is maintained by a regulator. For the boiler as the system, simplify the general energy balance as much as possible by deleting as many terms as feasible.
- Calculate Q for the system shown in Figure SAT22.5 P2.

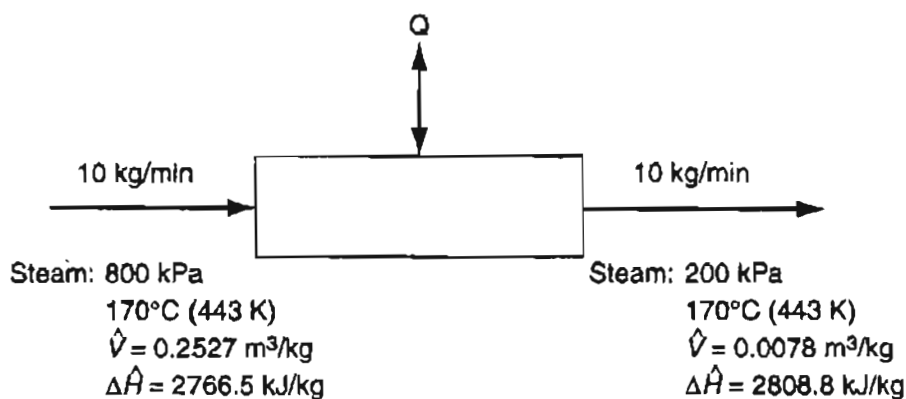


Figure SAT22.5P2

- A 13 MW steam-driven turbine operates in the steady state using 20 kg/s of steam. The inlet conditions for the steam are $p = 3000$ kPa and 450°C . The outlet conditions are

500 kPa, saturated vapor. The entering velocity of the steam is 250 m/s and the exiting velocity is 40 m/s. What is the heat transfer in kW for the turbine as the system? What fraction is the heat transfer of the power generated?

Thought Problems

1. During flow through a partially opened valve the temperature of the fluid drops from 30 to -30 degrees Celsius. Can the process occur adiabatically?
2. Would the temperature of air drop as it passes through a cracked valve in steady flow?
3. Would the temperature of a liquid drop as it passes through a cracked valve in steady flow?
4. If an air compressor operates as a steady-state system, compare the volumetric flow rates of the input and the output streams.
5. Will the outlet temperature of the gas in an adiabatic compressor be higher or lower than the inlet temperature of the gas? Explain your answer.

Discussion Problems

1. Why is a throttling valve commonly used in refrigeration and air conditioning equipment?
2. William Thompson (later Lord Kelvin) met Joule on the latter's honeymoon in the valley of Chamonix, Switzerland. Joule had a long thermometer to use in testing his theory that there should be a difference in the temperature at the top and bottom of a neighboring waterfall because of the dissipation of kinetic energy. This chance encounter cemented a warm friendship and a lifelong collaboration. Do you think Joule could have demonstrated the correctness of his theory in the indicated way?

Looking Back

In this chapter we formulated the general energy balance for four categories of processes: (1) closed, unsteady-state systems, (2) closed, steady-state systems, (3) open, unsteady-state systems, (4) open, steady-state systems. Worked examples in each category showed how to simplify the general energy balance and solve problems using the appropriate simplifications.

GLOSSARY OF NEW WORDS

Conservation of energy The total energy of a system plus its surroundings is constant.

General energy balance The change of energy inside a system is equal to the net heat and net work interchange with the surrounding plus the net energy transported by mass flow into and out of the system.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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Web Sites

<http://potoff1.eng.wayne.edu/che2800/notes/energy.pdf>

<http://www.che.uteledo.edu/meb/>

http://www.che.utexas.edu/cache/trc/t_material.html

PROBLEMS

***22.1** Consider the following systems:

- (a) Open system, steady state
- (b) Open system, unsteady state
- (c) Closed system, steady state
- (d) Closed system, unsteady state

For which system(s) can energy cross the system boundary?

***22.2** Draw a picture of the following processes, draw a boundary for the system, and state for each whether heat transfer, work, a change in internal energy, a change in enthalpy, a change in potential energy, and a change in kinetic energy occurs *inside the system*. Also classify each system as open or closed, and as steady state or unsteady state.

- (a) A pump, driven by a motor, pumps water from the first to the third floor of a building at a constant rate and temperature. The system is the pump.

- (b) As in (a) except the system is the pump and the motor.
- (c) A block of ice melts in the sun. The system is the block of ice.
- (d) A mixer mixes a polymer into a solvent. The system is the mixer.

***22.3** Explain specifically what the system is for each of the following processes; indicate if any energy transfer takes place by heat or work (use the symbols Q and W , respectively) or if these terms are zero.

- (a) A liquid inside a metal can, well insulated on the outside of the can, is shaken very rapidly in a vibrating shaker.
- (b) A motor and propeller used to drive a boat.
- (c) Water flows through a pipe at 1.0 m/min, and the temperature of the water and the air surrounding the pipe are the same.

***22.4** Draw a simple sketch of each of the following processes, and, in each, label the system boundary, the system, the surroundings, and the streams of material and energy that cross the system boundary.

- (a) Water enters a boiler, is vaporized, and leaves as steam. The energy for vaporization is obtained by combustion of a fuel gas with air outside the boiler surface.
- (b) Steam enters a rotary steam turbine and turns a shaft connected to an electric generator. The steam is exhausted at a low pressures from the turbine.
- (c) A battery is charged by connecting it to a source of current.

***22.5** Is it possible to compress an ideal gas in a cylinder with a piston isothermally in an adiabatic process? Explain your answer briefly.

✓ ****22.6** By use of the steam tables, compute the numerical values for Q , W , ΔH , and ΔU for the complete process in which one pound of liquid water is initially confined in a capsule at 327.8°F and 100 psia within an evacuated vessel of 4.435 ft³ capacity; the capsule is then broken within the vessel allowing the water to escape into the evacuated vessel; and finally the water is brought to the initial temperature (327.8°F).

***22.7** In a closed system process, 60 Btu of heat is added to the system, and the internal energy of the system increases by 220 Btu. Calculate the work of the process.

***22.8** Water is heated in a closed pot on top of a stove while being stirred by a paddle wheel. During the process, 30 kJ of heat is transferred to the water, and 5 kJ of heat is lost to the surrounding air. The work done amounts to 500 J. Determine the final energy of the system if its initial internal energy was 10 kJ.

***22.9** A person living in a 4 m × 5 m × 5 m room forgets to turn off a 100-W fan before he leaves the room which is at 100 kPa, 30°C. Will the room will be cooler when he comes back after 5 hours assuming zero heat transfer? The heat capacity at constant volume for air is 30 kJ/kg mol.

***22.10** A vertical cylinder capped by a piston weighing 990 g contains 100 g of air at 1 atmosphere and 25°C. Calculate the the maximum possible final elevation of the piston if 100 J of work is used to raise the cylinder and its contents vertically. Assume that all of the work goes into raising the piston.

✓ ****22.11** Four kg of superheated steam at 700 kPa and 500 K are cooled in a tank to 400 K. Calculate the heat transfer involved.

- *22.12** Two tanks are suspended in a constant temperature bath at 200°F . The first tank contains 1 ft^3 of dry saturated steam. The other tank is evacuated. The two tanks are connected. After equilibrium is reached, the pressure in both tanks is 1 psia . Calculate (a) the work done in the process, (b) the heat transfer to the two tanks, (c) the internal energy change of the steam, and (d) the volume of the second tank.
- ***22.13** A quantity of an ideal gas goes through the ideal cycle shown in Figure P22.13. Calculate:

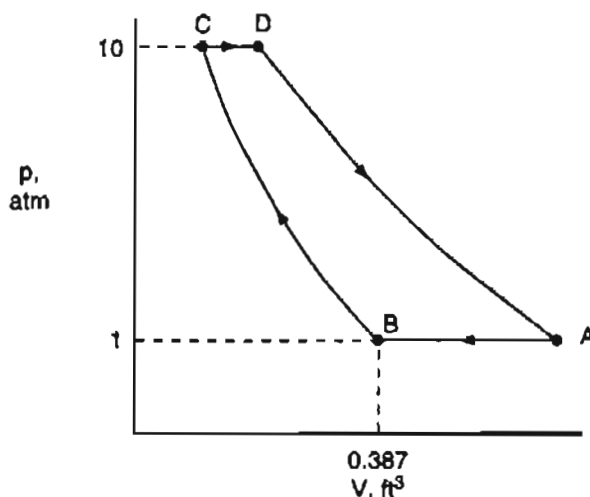


Figure P22.13

- Pound moles of gas being processed.
- V_D , ft^3
- W_{AB} , Btu
- W_{BC} , Btu
- W_{CD} , Btu
- W_{DA} , Btu
- W for the cycle, Btu
- ΔH for the cycle, Btu
- Q for the cycle, Btu

Data:

$$T_A = 170^{\circ}\text{F} \quad T_D = 823^{\circ}\text{F}$$

$$T_B = 70^{\circ}\text{F}$$

BC = isothermal process

DA = adiabatic process

Assume $C_V = 5/2 R$

- ✓**22.14** A cylinder contains 1 lb of steam at 600 psia and a temperature of 500°F . It is connected to another equal-sized cylinder which is evacuated. A valve between the cylinders is opened. If the steam expands into the empty cylinder, and the final temperature of the steam in both cylinders is 500°F , calculate Q , W , ΔU , and ΔH for the system comprised of both cylinders.
- *22.15** Two states, 1 and 2, are marked in P22.15. Path A is taken from 1 to 2. Two alternative return paths from 2 to 1 are shown: B and C. Two different cycles can now be

made up, each going from point 1 to point 2, and then returning to point 1. One cycle is made up from path A and path B, and the other from path A and path C. Are the following equations correct

$$Q_A + Q_B = W_A + W_B$$

$$Q_A + Q_C = W_A + W_C$$

for the cycle 1 to 2 and return?

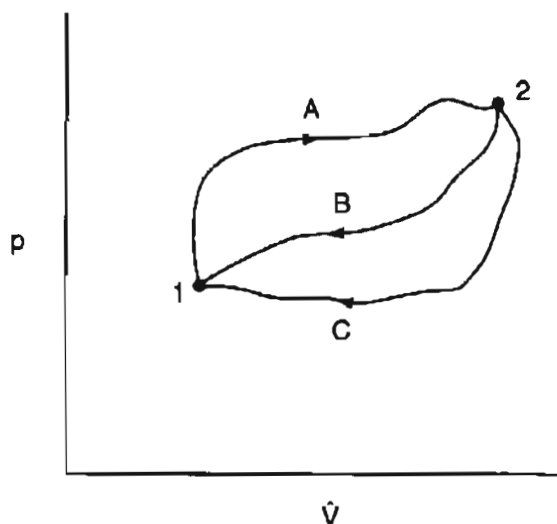


Figure P22.15

- *22.16** A national mail-order firm is advertising for \$699.99 ("manufacturer's suggested retail price \$1,199.00") the Cold Front Portable Air Conditioner, a "free-standing portable unit" which "does not require outside venting." It is intended to be rolled from room to room by the user, who simply plugs it into an ordinary 110-V AC outlet and enjoys the cool air from its "Cold Front." It is claimed to provide 5500 Btu/hour cooling capacity for 695 watts power. Is the cooling capacity correct? What is the catch to the advertisement?
- *22.17** A large high pressure tank contains 10 kg of steam. In spite of the insulation on the tank it loses 2050 kJ/hr to the surroundings. How many kW are needed to maintain the steam at 3000 kPa and 600 K?
- *22.18** An expensive drug is manufactured in a sealed vessel that holds 8 lb of water at 100°F. A $\frac{1}{4}$ hp motor stirs the contents of the vessel. What is the rate of heat removal from the vessel in Btu/min to maintain the temperature at 100°F?
- **22.19** Calculate how much heat is needed to evaporate 1 kg of water in an open vessel if the water starts at 27°C. Use the steam tables. The barometer reads 760 mm Hg.
- **22.20** Calculate Q , W , ΔU , and ΔH for 1 lb of liquid water which is evaporated at 212°F by (a) a non-flow process, and (b) a unsteady state flow process.
- ✓ ****22.21** A cylinder that initially contains nitrogen at 1 atm and 25°C is connected to a high pressure line of nitrogen at 50 atm and 25°C. When the cylinder pressure reaches 40 atm, the valve on the cylinder is closed. Assume the process is adiabatic, and that ni-

trogen can be treated as an ideal gas. What is the temperature in the cylinder when the valve is closed? Ideal heat capacities are listed in Table 23.1.

- *22.22** An insulated tank having a volume of 50 ft^3 contains saturated steam at 1 atm. It is connected to a steam line maintained at 50 psia and 291°F . Steam flows slowly into the tank until the pressure reaches 50 psia. What is the temperature in the tank at that time? Hint: Use the steam tables in the CD to make this an easy problem.
- **22.23** On a cold (5°F) day 30 gallon per minute of water is being pumped from a well to a storage tank 100 ft above the level of the water in the well. The temperature of the well water is 35°F . Although the storage tank and water lines are insulated, they still lose 5,000 Btu/hr to the air. To avoid having the water freeze, a heater puts 1000 Btu/min into the water line. The motor that operates the water pump is 5 hp and 30% efficient, i.e., 30% of the energy goes into the water and the rest is dissipated to the air. If the storage tank is initially empty, what is the temperature of the water in the tank after one hour. You can assume the storage tank is vented to the atmosphere if you want.
- *22.24** Start with the general energy balance, and simplify it for each of the processes listed below to obtain an energy balance that represents the process. Label each term in the general energy balance by number, and list by their numbers the terms retained or deleted followed by your explanation. (You do not have to calculate any quantities in this problem.)
- One hundred kilograms per second of water is cooled from 100°C to 50°C in a heat exchanger. The heat is used to heat up 250 kg/s of benzene entering at 20°C . Calculate the exit temperature of benzene.
 - A feedwater pump in a power generation cycle pumps water at the rate of 500 kg/min from the turbine condensers to the steam generation plant, raising the pressure of the water from 6.5 kPa to 2800 kPa. If the pump operates adiabatically with an overall mechanical efficiency of 50% (including both pump and its drive motor), calculate the electric power requirement of the pump motor (in kW). The inlet and outlet lines to the pump are of the same diameter. Neglect any rise in temperature across the pump due to friction (i.e., the pump may be considered to operate isothermally).
- *22.25** It is necessary to evaluate the performance of an evaporator that will be used to concentrate a 5% organic solution. Assume there will be no boiling point rise. The following information has already been obtained: $U = 300 \text{ Btu}/(\text{hr})(\text{ft}^2)(^\circ\text{F})$;

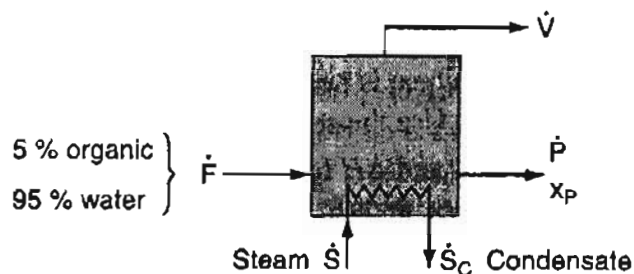


Figure P22.25

$A = 2,000 \text{ ft}^2$; heating steam S is available at 4.5 psia; feed enters at 140°F . Must any further measurements be made? The rate of heat transfer from the steam coils to the liquid is $\dot{Q} = UA(T_S - T_V)$.

- *22.26** Air is being compressed from 100 kPa and 255 K (where it has an enthalpy of 489 kJ/kg) to 1000 kPa and 278 K (where it has an enthalpy of 509 kJ/kg). The exit velocity of the air from the compressor is 60 m/s. What is the power required (in kW) for the compressor if the load is 100 kg/hr of air?

- *22.27** Write the simplified energy balance for the following processes:

- A fluid flows steadily through a poorly designed coil in which it is heated from 170° to 250°F . The pressure at the coil inlet is 120 psia, and at the coil outlet is 70 psia. The coil is of uniform cross section, and the fluid enters with a velocity of 2 ft/sec.
- A fluid is allowed to flow through a cracked (slightly opened) valve from a region where its pressure is 200 psia and 670°F to a region where its pressure is 40 psia, the whole operation being adiabatic.

List each assumption or decision by number. You do not have to solve the problems.

- *22.28** Write the appropriate simplified energy balances for the following changes; in each case the amount of material to be used as a basis of calculation is 1 lb and the initial condition is 100 psia and 370°F :

- The substance, enclosed in a cylinder fitted with a movable frictionless piston, is allowed to expand at constant pressure until its temperature has risen to 550°F .
- The substance, enclosed in a cylinder fitted with a movable frictionless piston, is kept at constant volume until the temperature has fallen to 250°F .
- The substance, enclosed in a cylinder fitted with a movable frictionless piston, is compressed adiabatically until its temperature has risen to 550°F .
- The substance, enclosed in a cylinder fitted with a movable frictionless piston, is compressed at constant temperature until the pressure has risen to 200 psia.
- The substance is enclosed in a container which is connected to a second evacuated container of the same volume as the first, there being a closed valve between the two containers. The final condition is reached by opening the valve and allowing the pressures and temperatures to equalize adiabatically.

- *22.29** Your company produces small power plants that generate electricity by expanding waste process steam in a turbine. You are asked to study the turbine to determine if it is operating as efficiently as possible. One way to ensure good efficiency is to have the turbine operate adiabatically. Measurements show that for steam at 500°F and 250 psia.

- The work output of the turbine is 86.5 hp.
- The rate of steam usage is 1000 lb/hr.
- The steam leaves the turbine at 14.7 psia and consists of 15 percent moisture (i.e., liquid H_2O).

Is the turbine operating adiabatically? Support your answer with calculations.

- **22.30** In one stage of a process for the manufacture of liquid air, air as a gas at 4 atm abs. and 250 K is passed through a long, insulated 3-in. ID pipe in which the pressure

drops 3 psi because of frictional resistance to flow. Near the end of the line, the air is expanded through a valve to 2 atm abs. State all assumptions.

- (a) Compute the temperature of the air just downstream of the valve.
- (b) If the air enters the pipe at the rate of 100 lb/hr, compute the velocity just downstream of the valve.

✓**22.31 A liquid that can be treated as water is being well mixed by a stirrer in a 1 m³ vessel. The stirrer introduces 300 watts of power into the vessel. The heat transfer from the tank to the surroundings is proportional to the temperature difference between the vessel and the surroundings (which are at 20°C). The flow rate of liquid in and out of the tank is 1 kg per minute. If the temperature of the inlet liquid is 40°C, what is the temperature of the outlet liquid? The proportionality constant for the heat transfer is 100 W/°C.

✓**22.32 Air is used to heat an auditorium. The flow rate of the entering air to the heating unit is 150 m³ per minute at 17°C and 100 kPa. The entering air passes through a heating unit that uses 15 kW for the electric coils. If the heat loss from the heating unit is 200 W, what is the temperature of the exit air?

**22.33 The following problem and its solution were given in a textbook:

How much heat in kJ is required to vaporize 1.00 kg of saturated liquid water at 100°C and 101.3 kPa? The solution is

$$n = 1.00 \text{ kg}$$

$$\Delta E = Q + W + E_{\text{flow}}$$

$$\Delta U = Q + W = Q - p\Delta V$$

$$Q = \Delta H = (1\text{kg})(2256.9\text{kJ/kg}) = 2256.9\text{kJ}$$

Is this solution correct?

*22.34 A turbine that uses steam drives an electric generator. The inlet steam flows through a 10 cm diameter pipe to the turbine at the rate of 2.5 kg/s at 600°C and 1000 kPa. The exit steam discharges through a 25 cm diameter pipe at 400°C and 100 kPa. What is the expected power obtained from the turbine if it operates essentially adiabatically?

CHAPTER 23

CALCULATION OF ENTHALPY CHANGES

23.1 Phase Transitions	682
23.2 Heat Capacity Equations	690
23.3 Tables and Charts to Retrieve Enthalpy Values	699
23.4 Computer Databases	705

Your objectives in studying this chapter are to be able to:

1. Locate data needed for energy balances.
2. Calculate enthalpy (and internal energy) changes from heat capacity equations, graphs and charts, tables, and computer databases given the initial and final states of the material.
3. Use the steam tables in both SI and AE units to obtain values for enthalpy and internal energy given values for two independent state properties.
4. Ascertain the reference state for enthalpy and internal energy in the data source.
5. Fit empirical heat capacity data with a suitable function of temperature by estimating the values of the coefficients in the function.
6. Convert an expression for the heat capacity from one set of units to another.
7. Appreciate the accuracy of the data you use.

This chapter is somewhat of a diversion from the path of explaining how to apply energy balances. We have found that students stumble in solving energy balance problems not because the concept is difficult to apply but because they are hampered by the lack of experience and facility in collecting and manipulating data to use in the equations. You will find that

The devil is in the details.

Looking Ahead

In this chapter we explain how you can look up and/or calculate values of the enthalpy and internal energy to use in energy balances. We will look at five sources of retrieving enthalpy data:

1. Equations to estimate the enthalpy of a phase transition
2. Heat capacity and other equations
3. Tables
4. Enthalpy charts
5. Computer databases

Enthalpies can also be *estimated* by generalized methods based on the theory of corresponding states or additive bond contributions, but we will not discuss these methods. Refer instead to the references at the end of the chapter for information.

Information is information, not matter or energy.

Norbert Wiener

23.1 Phase Transitions

Do you recall from Chapter 16 that **phase transitions** occur from the solid to the liquid phase, and from the liquid to the gas phase, and the reverse? During these transitions very large changes in the value of the enthalpy (and internal energy) for a substance occur, changes called **latent heat** changes, because they occur without any noticeable change in temperature. Because of the relatively large enthalpy change associated with phase transitions, it is important to accurately ascertain latent heats when applying energy balances that involve them. For a single phase, the enthalpy varies as a function of the temperature, as illustrated in Figure 23.1. The enthalpy changes that take place within a single phase are often called “**sensible heat**” changes.

The enthalpy changes for the phase transitions are termed **heat of fusion** (for melting), ΔH_{fusion} , and **heat of vaporization** (for vaporization), ΔH_v . The word “heat” has been carried along by custom from very old experiments in which enthalpy changes were calculated from experimental data that frequently involved heat transfer. Enthalpy of fusion and vaporization would be the proper terms, but they are not widely used. **Heat of condensation** is the negative of the heat of vaporization and the **heat of solidification** is the negative of the heat of fusion. The **heat of sublimation** is the enthalpy change from solid directly to vapor.

The overall enthalpy change of a pure substance, as illustrated in Figure 23.1, can be formulated as follows (per unit mass starting below the fusion temperature):

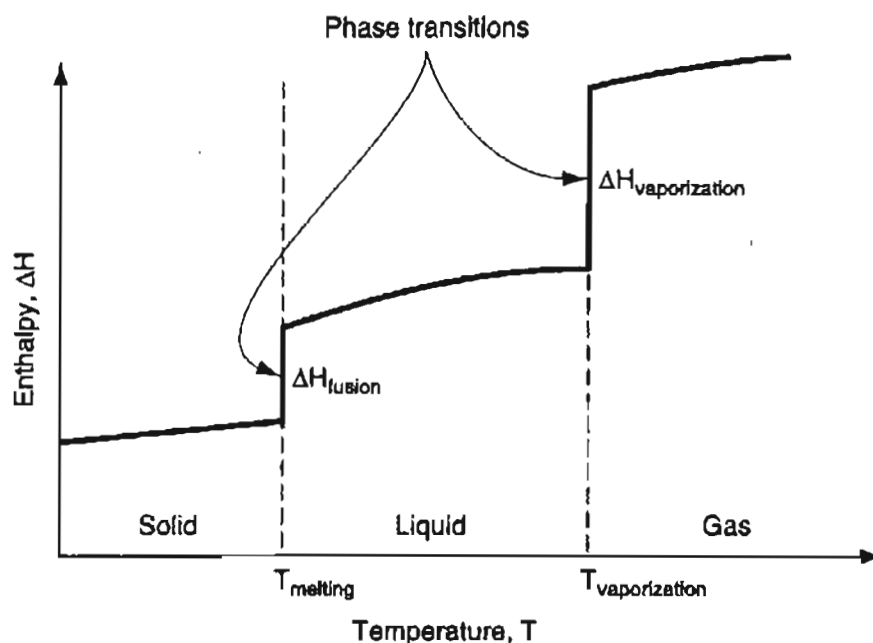


Figure 23.1 Enthalpy changes of a pure substance as a function of temperature. The vertical lines represent the “latent changes” that occur during a phase transition.

$$\begin{aligned}
 \Delta \hat{H} = \hat{H}(T) - \hat{H}(T_{\text{ref}}) = & \overset{\text{Sensible heat of solid}}{\int_{T_{\text{ref}}}^{T_{\text{fusion}}} C_{p, \text{solid}} dT} + \overset{\text{Melting}}{\Delta \hat{H}_{\text{fusion at } T_{\text{fusion}}}} + \overset{\text{Sensible heat of liquid}}{\int_{T_{\text{fusion}}}^{T_{\text{vaporization}}} C_{p, \text{liquid}} dT} \\
 & \overset{\text{Vaporization}}{+ \Delta \hat{H}_{\text{vaporization at } T_{\text{vap}}}} + \overset{\text{Sensible heat of vapor}}{\int_{T_{\text{vap}}}^T C_{p, \text{vapor}} dT} \quad (23.1)
 \end{aligned}$$

In tables such as the steam tables, all of the respective enthalpy changes shown in Equation (23.1), including the phase transitions, are built into the tabulated data. Changes in $\Delta \hat{U}$ can be calculated by an equation analogous to Equation (23.1) with C_v substituted for C_p , and values of the internal energy phases transitions substituted for the values of the enthalpies of the phase transitions.

Where can you get values for the enthalpies of phase changes? A few values of $\Delta \hat{H}$ for phases changes are listed in Appendix D, and over 700 are on the CD that accompanies this book. Other sources are experimental data and prediction methods cited in reference books listed in the supplementary references at the end of this chapter. You can also estimate values for $\Delta \hat{H}_v$ from some of the relations below. Use of experimental values for the heat of vaporization is recommended whenever

possible, but in the absence of the appropriate experimental values, one of the following methods can be used to estimate the heat of vaporization.

Equations to Estimate Heats of Vaporization

1. The Clapeyron Equation The Clapeyron equation is an exact thermodynamic relationship between the slope of the vapor-pressure curve and the molar heat of vaporization and the other variables listed below:

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)} \quad \text{or} \quad \frac{dp^*}{d(\ln T)} = \frac{\Delta \hat{H}_v}{\hat{V}_g - \hat{V}_l} \quad (23.22)$$

where p^* = vapor pressure

T = absolute temperature

$\Delta \hat{H}_v$ = molar heat of vaporization at T

\hat{V}_i = molar volume of gas or liquid as indicated by the subscript g or l

Figure 23.2 shows how the value of the slope $dp/d(\ln T)$ can be used to estimate the specific heat of vaporization. Any consistent set of units may be used.

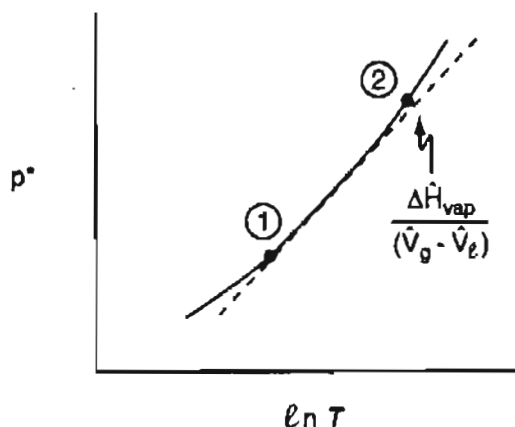


Figure 23.2 $\Delta \hat{H}_v$ is directly related to the slope of the plot of p^* versus $\ln T$, and varies with T .

Equation (23.2) can be used to calculate $\Delta \hat{H}_v$, and to check the internal consistency of data if a function for the vapor pressure of a substance is known so that you can evaluate dp^*/dT . If you assume that

(a) \hat{V}_l is negligible in comparison with \hat{V}_g .

(b) The ideal gas law is applicable for the vapor: $\hat{V}_g = RT/p^*$

Then

$$d \ln p^* = \frac{dp^*}{p^*} = \frac{\Delta \hat{H}_v dT}{RT^2} \quad (23.3)$$

If you further assume that $\Delta \hat{H}_v$ is constant over the temperature range of interest, integration of Equation (23.3) yields the **Clausius-Clapeyron equation**

$$\log_{10} \frac{p_1^*}{p_2^*} = \frac{\Delta \hat{H}_v}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (23.4)$$

Alternately, you can differentiate Antoine's equation to get $d \ln(p^*)/d\left(\frac{1}{T}\right)$ and combine Antoine's equation with Equation (23.2) to get ΔH_v .

2. Chen's Equation An equation that yields values of $\Delta \hat{H}_v$ (in kJ/g mol) to within 2% is Chen's equation*:

$$\Delta H_v = RT_b \left(\frac{3.978 (T_b/T_c) - 3.938 + 1.555 \ln p_c}{1.07 - (T_b/T_c)} \right) \quad (23.5)$$

where T_b is the normal boiling point of the liquid in K, T_c is the critical temperature in K, and p_c is the critical pressure in atmospheres.

3. Riedel's Equation**

$$\Delta H_v = 1.093RT_c \left[\frac{T_b}{T_c} \frac{(\ln p_c - 1)}{(0.930 - (T_b/T_c))} \right] \quad (23.6)$$

4. Watson's Equation Watson† found empirically that below the critical temperature the ratio of two heats of vaporization could be related by

$$\frac{\Delta \hat{H}_{v_2}}{\Delta \hat{H}_{v_1}} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38} \quad (23.7)$$

where $\Delta \hat{H}_{v_1}$ = heat of vaporization of a pure liquid at T_1

$\Delta \hat{H}_{v_2}$ = heat of vaporization of the same liquid at T_2

Yaws*** lists other values of the exponent for various substances.

The physical property software on the CD that accompanies this book provides the heat of vaporization at the normal boiling point (1 atm pressure). Therefore, it is recommended that when you need a heat of vaporization for an energy balance calculation, you use the heat of vaporization at the normal boiling point from the physical property software, and use Equation (23.7) to adjust for temperature difference from the normal boiling point.

*Chen, N. H. *Ind. Eng. Chem*, **51**, 1494 (1959).

Riedel, L. *Chem. Ing. Tech.*, **26, 83 (1954).

†K. M. Watson. *Ind. Eng. Chem.*, **23**, 360 (1931); **35**, 398 (1943).

***Yaws, C. L., H. C. Yang, and W. A. Cawley. "Predict Enthalpy of Vaporization," *Hydrocarbon Processing*, 87-90 (June 1990).

For example, let's use the heat of vaporization of water at 100°C for which $\Delta \hat{H}_v = 2256.1 \text{ kJ/kg}$ to calculate the heat of vaporization of water at 600 K. For water, $T_c = 647.4 \text{ K}$:

$$\frac{\Delta \hat{H}_{v, 600}}{\Delta \hat{H}_{v, 373}} = \left[\frac{(1 - \frac{600}{647.4})}{(1 - \frac{373}{647.4})} \right]^{0.38} = 0.551$$

$$\Delta \hat{H}_{v, 600} = 1244 \text{ kJ/kg}$$

The value for the heat of vaporization from the steam tables at 600 K is 1172.5 kJ/kg.

You can locate suggestions as to how to estimate all sorts of variables in the references at the end of this chapter.

5. Reference substance plots (Othmer, D. F., and H. T. Chen. *Ind. Eng. Chem.*, 60, 39–61 [1968]) can be used to estimate values for phase transitions (and numerous other properties). You saw an example of such a plot, the Cox chart, in Chapter 16. All you need are values for two points to fix a straight line for the property of interest once the scales on the vertical and horizontal axes are determined by making the property of interest a straight line for the reference substance.

EXAMPLE 23.1 Graph Showing the Heat of Vaporization of Water

Prepare a graph in which $\Delta \hat{H}$ in kJ/kg is plotted as a function of the temperature in °C for water starting at 90°C saturated liquid and stopping at 110°C saturated vapor.

Solution

Select data from the steam tables on the CD in the back of this book. The plot looks like Figure E23.1. The heat of vaporization is the vertical displacement at 100°C.

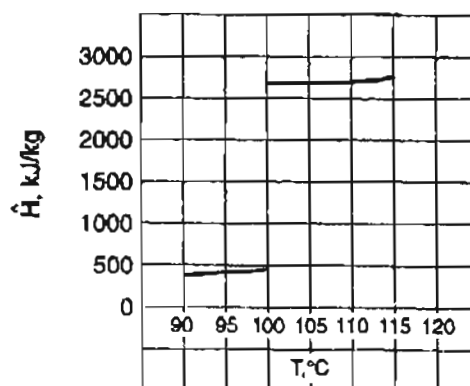


Figure E23.1

EXAMPLE 23.2 Comparison of Various Sources to Estimate the Heat of Vaporization

Use (a) the Clausius-Clapeyron equation, (b) Chen's equation, and (c) Riedel's equation to estimate the heat of vaporization of acetone at its normal boiling point, and compare with the experimental value of 30.2 kJ/g mol listed in Appendix C.

Solution

The basis is 1 g mol. You have to look up some data for acetone in Appendix D:

Normal boiling point: 329.2 K

T_c : 508.0 K

p_c : 47.0 atm

The next step is to calculate some of the values of the variables in the estimation equations

$$T_b/T_c = \frac{329.2}{508.0} = 0.648$$

$$\ln p_c = \ln(47.0) = 3.85$$

Using the Clayperon equation plus Antoine's equation:

From Equation (23.2)

$$d \ln(p^*) = \frac{\Delta \hat{H}_v dT}{RT^2} \quad (a)$$

and differentiating the Antoine equation

$$d \ln(p^*) = \frac{B}{(C + T)^2} dT \quad (b)$$

Combination of Equations (a) and (b) gives

$$\Delta H_v = \frac{RBT^2}{(C + T)^2} \quad (c)$$

From Appendix G

$$B = 2940.46 \quad C = -35.93$$

$$\begin{aligned} \Delta H_v &= \frac{8.314 \times 10^{-3}}{1} \left| \frac{2940.46}{(-35.93 + 329.2)^2} \right| \frac{(329.2)^2}{1} \\ &= 29.63 \text{ kJ/g mol} \quad (\text{low by 1.9\%}) \end{aligned}$$

Using Chen's equation:

From Equation (23.5)

$$\Delta H_v = \frac{8.314 \times 10^{-3} \text{ kJ}}{(\text{g mol})(\text{K})} \left| \frac{329.2 \text{ K}}{1.07 - 0.648} \right| \left[\frac{[(3.978)(0.648) - 3.938 + (1.555)(3.85)]}{1.07 - 0.648} \right]$$

$$= 30.0 \text{ kJ/g mol} \quad (\text{insignificant error})$$

Using Riedel's equation:

From Equation (23.6)

$$\Delta H_v = 1.093(8.314 \times 10^{-3})(508.0) \left[(0.648) \frac{(3.85 - 1)}{(0.930 - 0.648)} \right]$$

$$= 30.23 \text{ kJ/g mol} \quad (\text{negligible error})$$

SELF-ASSESSMENT TEST

Questions

- Answer the following questions true or false:
 - The molar heat of vaporization of water is 40.7 kJ/g mol.
 - The molar heat of vaporization you look up in a reference book or database come from experimental data.
 - The molar heat of fusion is the amount of energy necessary to freeze 1 g mol of substance at its melting point.
- Define
 - heat of vaporization
 - heat of condensation
 - heat of transition
- Why do engineers use the term "heat of" for the energy change that occurs in a phase transition rather than the better term "enthalpy change"?

Problems

- Ethane (C_2H_6) has a heat of vaporization of 14.707 kJ/g mol at 184.6 K. What is the estimated heat of vaporization of ethane at 210 K?
- At 0°C you melt 315 g of H_2O . What is the energy change corresponding to the process?
- One hundred g of H_2O exists in the gas phase at 395 K. How much energy will it take to condense all of the H_2O at 395 K?

Thought Problems

1. A fire-induced BLEVE (boiling liquid expanding vapor explosion) in a storage tank can result in a catastrophe. The scenario is somewhat as follows: A pressure vessel (e.g., a pressurized storage tank), partially filled with liquid, is subjected to high heat flux from a fire. The temperature of the liquid starts to increase, causing an increase in pressure within the tank. When the vapor pressure reaches the safety relief valve pressure setting, the relief valve opens and starts to vent vapor (or liquid) to the outside. Concurrent with the previous step, the temperature of the portion of the tank shell not in contact with the liquid (i.e., the ullage space) increases dramatically.

The heat weakens the tank shell around the ullage space. Thermally induced stresses are created in the tank shell near the vapor/liquid interface, and the heat-weakened tank plus the high internal pressure combine to cause a sudden, violent tank rupture. Fragments of the tank are propelled away from the tank at great force. Most of the remaining superheated liquid vaporizes rapidly due to the pressure release. The rest is mechanically atomized to small drops due to the force of the explosion. A fireball is created by the burning vapor and liquid.

What steps would you recommend to prevent a BLEVE in the case of fire near a storage tank? [Hint: Two possible routes are: (1) prevent the fire from heating the tank; and (2) prevent the buildup of pressure in the tank.]

2. A tanker used in the construction of pavement was being filled with tar with a temperature of slightly less than 100°C . When half-full, the tar pump failed. To clear the inlet line of solid tar, the line was blown out with steam. The driver of the tanker went to another location to fill the tanker. A few seconds after the filling commenced, hot tar erupted from the tanker manhole. Why did this occur?

Discussion Problems

1. An advertisement in the newspaper said you can buy a can of instant car cooler from which you spray the product inside a car to reduce the temperature. The spray consists of a mixture of ethanol and water. The picture in the advertisement shows a thermometer "before" registering 41°C and the thermometer "after" registering 27°C . Explain to the owner of Auto Sport, an auto parts retailer, whether or not he should buy a case of the spray cans from the distributor.
2. A fermentation tank fitted with a 5 cm open vent was sterilized with steam at 140°C for one-half an hour. Then the steam was shut off and the next batch of fluid was dumped into the tank. Shortly thereafter the tank imploded (burst inward). What is your explanation of the accident?
3. The use of a salt phase change is being proposed as a storage method for electricity-generating windmills is being studied. The concept involves a tank of NaNO_3 . In low demand periods, pipes inside the tank would be heated by electricity to melt the salt, and in

times of peak demand water flowing through the pipes would generate steam as the salt solidified. Would you recommend this process?

23.2 Heat Capacity Equations

You will recall that in Chapter 21 we explained that the enthalpy change for a substance in a single phase (**not for the phase transitions**) can be calculated using the **heat capacity**

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p dT \quad (23.8)$$

If C_p is constant, $\Delta \hat{H} = C_p \Delta T$ where $\Delta T = T_2 - T_1$.

Figure 23.3 illustrates how $\Delta \hat{H}$ is the area between two limits under the C_p function.

To give the heat capacity some physical meaning, you can think of C_p as representing the amount of energy required to increase the temperature of a substance by 1 degree, energy that might be provided by heat transfer in certain specialized processes, but can be provided by other means as well. For incompressible substances, $C_p = C_v$. For most liquids and solids, neither C_p nor C_v changes substantially with temperature at normal ambient temperatures, although $C_p \neq C_v$ in general. Because C_v is not used very often, we will restrict our discussion to C_p . What are the units of the heat capacity? From the definition of heat capacity in Chapter 21 you know that the units are (energy)/(unit temperature difference) (unit mass or moles), hence the term “specific heat” (capacity) is sometimes used for heat capacity.*

Calories don't count when they are at room temperature.

Cathy

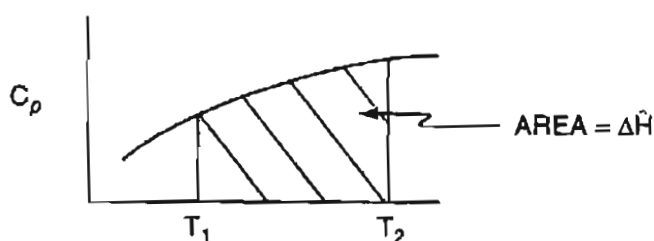


Figure 23.3 $\Delta \hat{H}$ interpreted as the area obtained by integrating $C_p(T)$ between two temperature limits.

*Some engineering books define “specific heat” as the ratio of a heat capacity of one substance to the heat capacity of a reference substance.

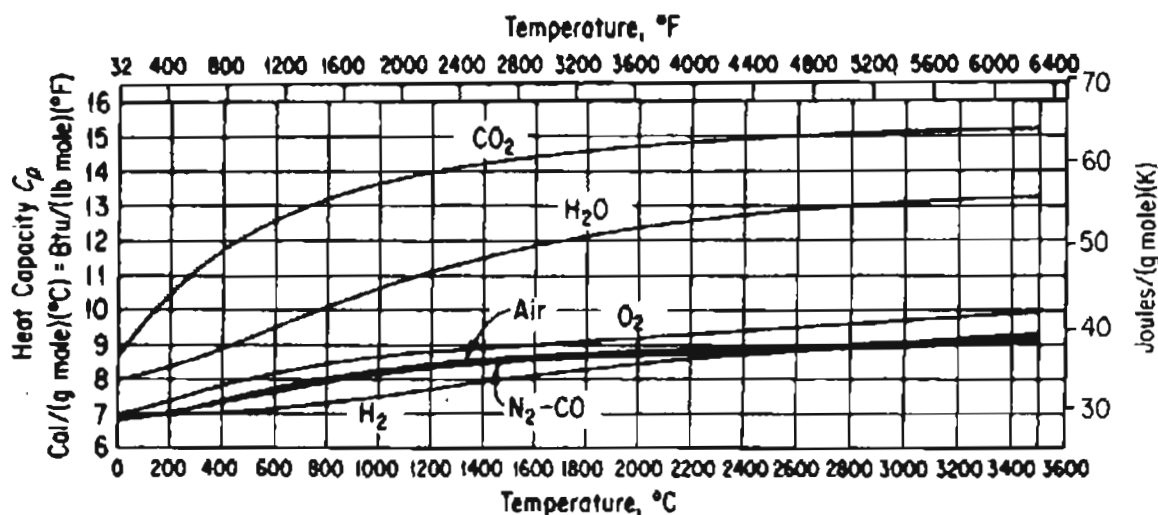


Figure 23.4 Heat capacity curves for the combustion gases.

The heat capacity varies with temperature for solids, liquids, and real gases, but is a continuous function of temperature only in the region between the phase transitions. Consequently, it is not possible to have a heat capacity equation for a substance that will go from absolute zero up to any desired temperature. Examine Figure 23.4 to see how C_p changes for several gases.

How are the functions in Figure 23.4 prepared? What you do is determine experimentally the heat capacity between the temperatures at which the phase transitions occur, and then fit the data with an equation. If you can assume the gas is an ideal gas, the heat capacity at constant pressure is constant even though the temperature varies (examine Table 23.1).

TABLE 23.1 Heat Capacities of Ideal Gases

Type of molecule*	Approximate heat capacity, C_p	
	High temperature (translational, rotational, and vibrational degrees of freedom)	Room temperature (translational and rotational degrees of freedom only)
Monoatomic	$\frac{5}{2}R$	$\frac{5}{2}R$
Polyatomic, linear	$\left(3n - \frac{3}{2}\right)R$	$\frac{7}{2}R$
Polyatomic, nonlinear	$(3n - 2)R$	$4R$

* n , number of atoms per molecule; R , gas constant.

For ideal gases a simple relation exists between C_p and C_v because U and H are functions of temperature only:

$$p\hat{V} = RT$$

$$\hat{H} = \hat{U} + p\hat{V} = \hat{U} + RT$$

Differentiate \hat{H} with respect to temperature

$$C_p = \left(\frac{d\hat{H}}{dT} \right) = \left(\frac{d\hat{U}}{dT} \right) + R = C_v + R \quad (23.9)$$

For ideal gas mixtures, the heat capacity (per mole) of the mixture is the mole-weighted average of the heat capacities of the components (x_i is the mole fraction of component i):

$$C_{p_{\text{avg}}} = \sum_{i=1}^n x_i C_{p_i} \quad (23.10)$$

For nonideal mixtures, particularly liquids, you should refer to experimental data or some of the estimation techniques listed in the literature (see the supplementary references at the end of this chapter).

Most of the equations for the heat capacities of solids, liquids, and gases are empirical. You usually find that the heat capacity at constant pressure, C_p , is expressed as a function of temperature for a specified range of temperature. A power series in temperature, with constants a , b , c , and so on, is typically used to model the temperature dependence of C_p . For example

$$C_p = a + bT + cT^2 \quad (23.11)$$

where the temperature may be expressed in degrees Celsius, degrees Fahrenheit, degrees Rankine, or degrees kelvin. Since the heat capacity equations are valid only over moderate temperature ranges, it is possible to have equations of different types represent the experimental heat capacity data with almost equal accuracy. **Be wary of extrapolation beyond the designated range of validity for C_p .** The task of fitting heat capacity equations to heat capacity data is greatly simplified by the use of commercial software, which can determine the constants of best fit and at the same time determine how precise the predicted heat capacities are. Appendix M explains how to use a procedure called least squares to get the coefficients in Equation (23.11) based on a set of C_p versus temperature values.

You will find heat capacity and enthalpy information for about 750 compounds, both gases and liquids, in the Appendices and in the CD in the back of this book (which is based on the work of Professor Yaws). You can also find sources of heat capacity data in several of the references listed at the end of this chapter and on

the Internet. The change of C_p at high pressures is beyond the scope of our work here.

When you cannot find a heat capacity for a gas, you can estimate one by using one of the numerous equations that can be found in the supplementary references at the end of this chapter. Estimation of C_p for liquids is fraught with error, but some relationships exist as well. For aqueous solutions, you can roughly approximate C_p by using the water content only.

Given the heat capacity equation, for example, Equation (23.11), you can calculate the enthalpy change per unit mole or mass by integrating the heat capacity equation with respect to temperature

$$\Delta \hat{H} = \int_{T_1}^{T_2} (a + bT + cT^2) dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \quad (23.12)$$

If you select a different functional form of the heat capacity than Equation (23.11), the integration result will have a different form, of course.

EXAMPLE 23.3 Conversion of Units in a Heat Capacity Equation

The heat capacity equation for CO_2 gas in the temperature range 0 to 1500 K is

$$C_p = 2.675 \times 10^4 + 42.27 T - 1.425 \times 10^{-2} T^2$$

with C_p expressed in $\text{J}/(\text{kg mol})(\Delta\text{K})$ and T in K. Convert this equation into a form so that the heat capacity will be expressed over the entire temperature range in $\text{Btu}/(\text{lb mol})(^\circ\text{F})$ with T in $^\circ\text{F}$.

Solution

Changing a heat capacity equation from one set of units to another is merely a problem in the *conversion of units*. Each term in the heat capacity equation must have the same units as the lefthand side of the equation. To avoid confusion in the conversion, you must remember to distinguish between the temperature symbol that in one usage represents temperature, and the usage of the same symbol to represent temperature difference. In the conversions below we shall distinguish between the temperature and the temperature difference for clarity, as was done in Chapter 5.

First, multiply each side of the given equation for C_p by appropriate conversion factors to convert $\text{J}/(\text{kg mol})(\Delta\text{K})$ to $(\text{Btu}/\text{lb mol})(\Delta^\circ\text{F})$. Multiply the lefthand side by the factor in the square brackets.

$$\frac{C_p \text{ J}}{(\text{kg mol})(\Delta\text{K})} \times \left[\frac{1 \text{ Btu}}{1055 \text{ J}} \left| \frac{1 \Delta\text{K}}{1.8 \Delta^\circ\text{R}} \right| \frac{1 \Delta^\circ\text{R}}{1 \Delta^\circ\text{F}} \left| \frac{0.4536 \text{ kg}}{1 \text{ lb}} \right| \right] \rightarrow C_p \frac{\text{Btu}}{(\text{lb mol})(\Delta^\circ\text{F})}$$

and multiply the righthand side by the same set of conversion factors.

Next, substitute the relation between the temperature in K and the temperature in °F

$$T_K = \frac{T_R}{1.8} = \frac{T_F + 460}{1.8}$$

into the given equation for C_p where T appears.

Finally, carry out the indicated mathematical operations, and consolidate quantities to get

$$C_p = 8.702 \times 10^{-3} + 4.66 \times 10^{-6} T_F - 1.053 \times 10^{-9} T_F^2$$

EXAMPLE 23.4 Fitting a Heat Capacity Equation to Heat Capacity Data

The heat capacity of carbon dioxide gas at 1 atm as a function of temperature has been found by a series of repeated experiments to be as follows:

T(K)	300	400	500	600	700	800
C_p [J/(g mol)(K)]	39.87	45.16	50.72	56.85	63.01	69.52
	39.85	45.23	51.03	56.80	63.09	69.68
	39.90	45.17	50.90	57.02	63.14	69.63

Find the values of the coefficients in the equation

$$C_p = a + bT + cT^2$$

that yield the best fit to the data.

Solution

The variables are a , b , and c . Use statistical software (or Polymath on the CD in the back of this book) to minimize the sum of the squares of the deviations between the predicted values of C_p and the experimental ones (refer to Appendix M for the procedure):

$$\text{Minimize } \sum_{i=1}^{18} (C_{p,\text{predicted},i} - C_{p,\text{experimental},i})^2$$

All 18 data points can be in the sum, or an average C_p at each temperature can be used instead, in which case the sum is over the six average values.

The solution is

$$C_p = 25.47 + 4.367 \times 10^{-2} T - 1.44 \times 10^{-5} T^2$$

Compare this equation with the heat capacity equation for carbon dioxide listed in Appendix E1.

EXAMPLE 23.5 Calculation of $\Delta\hat{H}$ for a Gas Mixture Using Heat Capacity Equations for Each Component

The conversion of solid wastes to innocuous gases can be accomplished in incinerators in an environmentally acceptable fashion. However, the hot exhaust gases often must be cooled or diluted with air. An economic feasibility study indicates that solid municipal waste can be burned to a gas of the following composition (on a dry basis):

CO ₂	9.2%
CO	1.5%
O ₂	7.3%
N ₂	82.0%
	<u>100.0%</u>

What is the enthalpy difference for this gas per lb mol between the bottom and the top of the stack if the temperature at the bottom of the stack is 550°F and the temperature at the top is 200°F? Ignore the water vapor in the gas. You can neglect any energy effects resulting from the mixing of the gaseous components.

Solution

Basis: 1 lb mol of gas

The heat capacity equations are [T in °F; C_p = Btu/(lb mol)(°F)]

$$\text{N}_2: C_p = 6.895 + 0.7624 \times 10^{-3} T - 0.7009 \times 10^{-7} T^2$$

$$\text{O}_2: C_p = 7.104 + 0.7851 \times 10^{-3} T - 0.5528 \times 10^{-7} T^2$$

$$\text{CO}_2: C_p = 8.448 + 5.757 \times 10^{-3} T - 21.59 \times 10^{-7} T^2 + 3.059 \times 10^{-10} T^3$$

$$\text{CO}: C_p = 6.865 + 0.8024 \times 10^{-3} T - 0.7367 \times 10^{-7} T^2$$

Basis: 1.00 lb mol of gas

By multiplying these equations by the respective mole fraction of each component, and then adding them together, you can save time in the integration, but they can be integrated separately. If you use the computer program in the CD that accompanies this book for calculating ΔH , you may involve a slightly different set of equations.

$$\text{N}_2: 0.82(6.895 + 0.7624 \times 10^{-3} T - 0.7009 \times 10^{-7} T^2)$$

$$\text{O}_2: 0.073(7.104 + 0.7851 \times 10^{-3} T - 0.5528 \times 10^{-7} T^2)$$

$$\text{CO}_2: 0.092(8.448 + 5.757 \times 10^{-3} T - 21.59 \times 10^{-7} T^2 + 3.059 \times 10^{-10} T^3)$$

$$\text{CO}: 0.015(6.865 + 0.8024 \times 10^{-3} T - 0.7367 \times 10^{-7} T^2)$$

$$C_{p_{\text{net}}} = 7.053 + 1.2242 \times 10^{-3} T - 2.6124 \times 10^{-7} T^2 + 0.2814 \times 10^{-10} T^3$$

$$\begin{aligned}
 \Delta H &= \int_{550}^{200} (7.053 + 1.2242 \times 10^{-3} T - 2.6124 \times 10^{-7} T^2 + 0.2814 \times 10^{-10} T^3) dT \\
 &= 7.053[(200) - (550)] + \frac{1.2242 \times 10^{-3}}{2} [(200)^2 - (550)^2] \\
 &\quad - \frac{2.6124 \times 10^{-7}}{3} [(200)^3 - (550)^3] + \frac{0.2814 \times 10^{-10}}{4} [(200)^4 - (550)^4] \\
 &= -2468.6 - 160.7 + 13.8 - 0.633 = -2616 \text{ Btu/lb mol gas}
 \end{aligned}$$

Now that you have become acquainted with both enthalpy changes for phase transitions and sensible heat, it is time to combine these concepts so that you can calculate enthalpy changes including phase changes. Look at Figure 23.5, which shows the transition of water from -30°C to 130°C .

We want to determine the value at 130°C of $\Delta \hat{H}$ on the vertical axis, starting with -30°C as the reference point of zero. As shown in Equation (23.1), you add the values of the enthalpies of the phase transition to the ΔH values for the sensible heats obtained by integrating the heat capacity equations for ice, liquid water, and water vapor, respectively.

$$\begin{aligned}
 \Delta \hat{H}_{T_{\text{ref}}}^{T_{\text{final}}} &= \hat{H}(T_{\text{final}}) - \hat{H}(T_{\text{ref}}) = \int_{T_{\text{ref}}}^{T_{\text{fusion}}} C_{p, \text{ice}} dT + \Delta \hat{H}_{\text{fusion}, 0^\circ\text{C}} \\
 &\quad + \int_{T_{\text{fusion}}}^{T_{\text{vaporization}}} C_{p, \text{liquid water}} dT + \Delta \hat{H}_{\text{vaporization}, 100^\circ\text{C}} \\
 &\quad + \int_{T_{\text{vaporization}}}^{T_{\text{final}}} C_{p, \text{water vapor}} dT
 \end{aligned} \tag{23.13}$$

For the case in Figure 23.5, $T_{\text{fusion}} = 0^\circ\text{C}$ and $T_{\text{vaporization}} = 100^\circ\text{C}$. Values of $\Delta \hat{H}_{\text{fusion}}$ and $\Delta \hat{H}_{\text{vaporization}}$ are shown in the figure.

Because $\Delta \hat{H}$ is a state variable, you know that you can calculate its value for the same beginning and ending states by any path. Thus, if you ignored any minor pressure effects and had adequate data for water, you could melt the ice at a temperature above or below 0°C , and vaporize the water above or below 100°C . We used 0°C and 100°C , respectively, as the transition temperatures because the values of the enthalpies at these temperatures are so well known.

Let's calculate the enthalpy change for 1 kg of water from -30°C to 130°C , using the data in Figure 23.5 plus values for C_p of

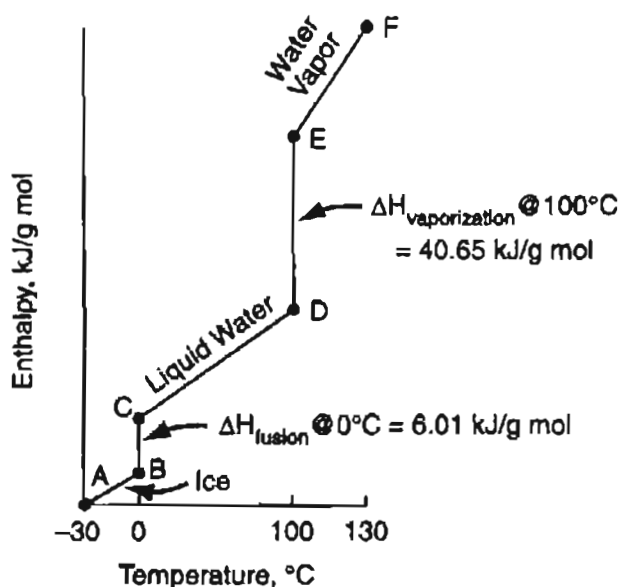


Figure 23.5 The change of enthalpy of water from -30°C to 130°C .

ice	23.7 J/g mol
liquid water	75.4 J/g mol
water vapor	33.9 J/g mol

You could use equations from the physical properties software on the CD in the back of this book, but for the purposes of illustration of the concept let's ignore slight changes of C_p over the short temperature ranges involved, and ignore any effect of pressure (which increases as the temperature increases).

$$\begin{aligned}\Delta \hat{H}_{-30^{\circ}\text{C}}^{130^{\circ}\text{C}} &= \hat{H}(130^{\circ}\text{C}) - \hat{H}(-30^{\circ}\text{C}) = (23.7)(0 - (-30)) + 6.01 + (75.4)(100 - 0) \\ &\quad + 40.65 + (33.9)(130 - 100) = 55,930 \text{ J/g mol}\end{aligned}$$

SELF-ASSESSMENT TEST

Questions

- Answer the following questions true or false:
 - For a real gas $\Delta H = \int_{T_1}^{T_2} C_p dT$ is an exact expression.
 - For liquids below $T_r = 0.75$ or a solid, $\Delta U \approx \int_{T_1}^{T_2} C_p dT$
 - For ideal gases near room temperature $C_p = 5/2R$.
 - C_v cannot be used to calculate $\Delta \hat{H}$ —you have to use C_p .
- Is the term specific energy a better term to use to represent specific heat?
- What is the heat capacity at constant pressure at room temperature of O_2 if the O_2 is assumed to be an ideal gas?

Problems

1. Determine the specific enthalpy of liquid water at 400 K and 500 kPa relative to the specific enthalpy value of liquid water at 0°C and 500 kPa using a heat capacity equation. Compare the value obtained from the steam tables.
2. A problem indicates that the enthalpy of a compound can be predicted by an empirical equation $\hat{H}(\text{J/g}) = -30.2 + 4.25 T + 0.001 T^2$, where T is in kelvin. What is a relation for the heat capacity at constant pressure for the compound?
3. A heat capacity equation in $\text{cal}/(\text{g mol})(\text{K})$ for ammonia gas is

$$C_p = 8.4017 + 0.70601 \times 10^{-2} T + 0.10567 \times 10^{-5} T^2 - 1.5981 \times 10^{-9} T^3$$

where T is in °C. What are the units of each of the coefficients in the equation?

4. Convert the following equation for the heat capacity of carbon monoxide gas, where C_p is in $\text{Btu}/(\text{lb mol})(^\circ\text{F})$ and T is in °F:

$$C_p = 6.865 + 0.08024 \times 10^{-2} T - 0.007367 \times 10^{-5} T^2$$

to yield C_p in $\text{J}/(\text{kg mol})(\text{K})$ with T in kelvin.

5. Calculate the enthalpy and internal energy changes in J/g mol that occur when N_2 is heated from 30°C to 300°C at one atmosphere.
6. Water vapor is cooled from 300°F to solid at 0°F. Use heat capacity values and phase transition values to compute $\Delta\hat{H}$ in Btu/lb for the change.

Thought Problems

1. A piece of wood and a piece of metal both having identical masses are removed from an oven after they reach the same temperature. Then each are placed on a block of ice. Which piece will melt the most ice when the piece reaches the ice temperature?
2. Textbooks often indicate that for solids and liquids the difference ($C_p - C_v$) is so small that you can say that ($C_p = C_v$). Is this generally true?
3. Fire walkers with bare feet walk across beds of glowing coals without apparent harm. The rite is found in many parts of the world today and was practiced in classical Greece and ancient India, according to the *Encyclopaedia Britannica*. Why are they not burned?
4. A given amount of gas in a closed container is heated from 25 to 50°C at 1 atm. The heating is carried out at a later time at 3 atm. In which case will the energy requirement be greater?

Discussion Problems

1. Dow Chemical sells Dowtherm Q, a heat transfer fluid that has an operating range of 30°F to 625°F, for \$12/gal. Dowtherm Q competes with mineral oil, which costs \$3/gal and operates up to 600°F. Why would a company pay so much more for Dowtherm Q?
2. In *Chemical Engineering Education* (Summer 1994), the question was asked as to why soldiers in the Middle Ages poured boiling oil on attacking enemy soldiers rather than

boiling water, especially when the heat capacity of oil is less than one-half of that of water. What would be the rationale for the use of oil?

23.3 Tables and Charts to Retrieve Enthalpy Values

The firewood lies there but every man must gather and light it himself.

The Lone Ranger

Tables listing smoothed experimental data can accurately cover ranges of physical properties well beyond the range applicable for a single equation. Because the most commonly measured properties are temperature and pressure, tables of enthalpies (and internal energies) for pure compounds usually are organized in columns and rows, with T and p being the independent variables. If the intervals between table entries are close enough, linear interpolation between entries is reasonably accurate. For example, look at the following extract from the SI Steam Tables. If you want to calculate the enthalpy of saturated steam at 307 K by linear interpolation, as explained in Chapter 16 in connection with the Steam Tables, you would carry out the following computation:

$$H_{307} = H_{305} + \frac{H_{310} - H_{305}}{T_{310} - T_{305}}(T_{307} - T_{305}) = 2559.1 + \frac{2568.2 - 2559.1}{310 - 305} = (307 - 305) = 2557.5$$

PROPERTIES OF SATURATED WATER

T K	Press. kPa	Volume, m ³ /kg		Enthalpy, kJ/kg		
		V _t	V _g	H _l	H _{vap}	H _g
273.16	0.6113	0.001000	206.1	0.0	2500.9	2500.9
275	0.6980	0.001000	181.7	7.5	2496.8	2504.3
280	0.9912	0.001000	130.3	28.1	2485.4	2513.5
285	1.388	0.001001	94.67	48.8	2473.9	2522.7
290	1.919	0.001001	69.67	69.7	2462.2	2531.9
295	2.620	0.001002	51.90	90.7	2450.3	2541.0
300	3.536	0.001004	39.10	111.7	2438.4	2550.1
305	4.718	0.001005	29.78	132.8	2426.3	2559.1
310	6.230	0.001007	22.91	153.9	2414.3	2568.2
315	8.143	0.001009	17.80	175.1	2402.0	2577.1
320	10.54	0.001011	13.96	196.2	2389.8	2586.0
325	13.53	0.001013	11.04	217.3	2377.6	2594.9
330	17.21	0.001015	8.809	238.4	2365.3	2603.7
335	21.71	0.001018	7.083	259.4	2353.0	2612.4
340	27.18	0.001021	5.737	280.5	2340.5	2621.0

In the examples below we will use two types of tables. The first set of tables are the tables that can be found in the back of this book in Appendix D for the enthalpies at 1 atm of selected gases. The second set of tables are the steam tables that you learned about in Chapter 16, which include phase transition data and the effects of pressure on enthalpies. Remember that enthalpy values are all relative to some reference state. You can calculate enthalpy differences by subtracting the initial enthalpy from the final enthalpy for any two sets of conditions, as shown in the following examples; the reference state cancels out.

At the end of this chapter you will find several sources that give tables of enthalpy values, and, of course, the CD in the back of this book calculates $\Delta\hat{H}$ and $\Delta\hat{U}$ for you.

With respect to the steam tables, and tables of properties of compounds found in handbooks and databases, you will find that in the two-phase region values for only the saturated liquid and saturated vapor are listed. You have to interpolate between these saturated liquid and vapor values to get properties of vapor-liquid mixtures as explained in Chapter 16. **For compressed liquids you can use the properties of the saturated liquid for the same temperature as a good approximation.** Look at the foldout listing the properties of liquid water in the back of this book to verify this statement.

EXAMPLE 23.6 Calculation of the Enthalpy Change of a Gas Using Tabulated Enthalpy Values

Calculate the enthalpy change for 1 kg mol of N_2 gas that is heated at a constant pressure of 100 kPa from 18°C to 1100°C.

Solution

Because 100 kPa is essentially 1 atm, you can use the tables in Appendix D6 to calculate the enthalpy change, or use the CD.

$$\text{At } 1100^\circ\text{C} \text{ (1373K): } \hat{H} = 34.715 \text{ kJ/kg mol (by interpolation)}$$

$$\text{At } 18^\circ\text{C} \text{ (291K): } \hat{H} = 0.524 \text{ kJ/kg mol}$$

Basis: 1 kg of N_2

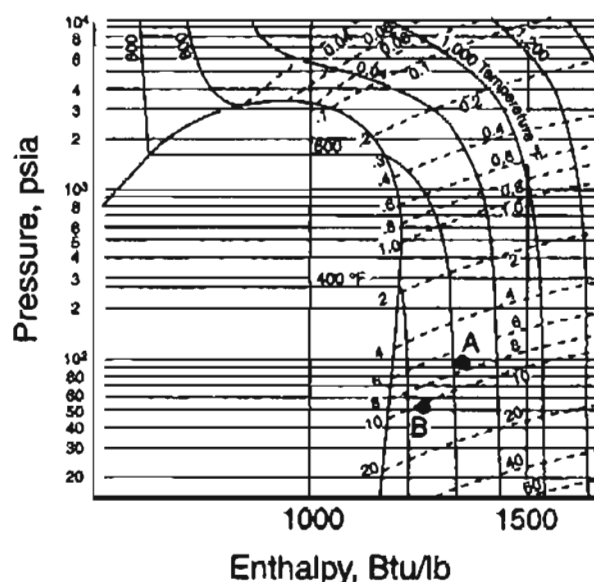
$$\Delta\hat{H} = 34.715 - 0.524 = 34.191 \text{ kJ/kg mol}$$

EXAMPLE 23.7 Use of the Steam Tables to Calculate Changes in Enthalpy

Steam is cooled from 640°F and 92 psia to 480°F and 52 psia. What is $\Delta \hat{H}$ in Btu/lb?

Solution

The problem asks for the change in \hat{H} from state A to state B as indicated in Figure E23.7.

**Figure E23.7**

Use the tables in the AE units in the foldout in the back of the book. You must employ double interpolation to get the specific enthalpies, \hat{H} (all are relative to the reference for the table). Values of \hat{H} are interpolated first between pressures at fixed temperature, and then between temperatures at fixed (interpolated) pressure.

$T(^{\circ}\text{F})$				$T(^{\circ}\text{F})$		
p (psia)	600	700	p	600	640	700
90	1328.7	1378.1	92	1328.6	1348.4	1378.0
95	1328.4	1377.8				
	400	500	p	450	480	500
50	1258.7	1282.6	52	1258.4	1272.8	1282.4
55	1258.2	1282.2				

Note that the steam table values include the effect of pressure on \hat{H} as well as temperature. An example of the interpolation carried out at 600°F that yielded the value of 1328.6 at 92 psia is

$$\frac{2}{5}(1328.7 - 1328.4) = 0.4(0.3) = 0.12$$

$$\text{At } p = 92 \text{ psia and } T = 600^\circ\text{F}, \hat{H} = 1328.7 - 0.12 = 1328.6.$$

The enthalpy change requested in the problem statement is

$$\Delta \hat{H} = 1272.8 - 1348.4 = -75.6 \text{ Btu/lb}$$

Note: If you use the CD that accompanies this book, you can avoid the interpolations.

EXAMPLE 23.8 Use of the Steam Tables When a Phase Change is Involved to Calculate the Final State of the Water

Four kilograms of water at 27°C and 200 kPa are heated at constant pressure until the volume of the water becomes 1000 times the original value. What is the final temperature of the water?

Solution

You can neglect the effect of pressure on the volume of liquid water (to check this assumption refer to the table of the properties of liquid water), hence the initial specific volume is that of saturated liquid water at 300 K, or 0.001004 m³/kg. The final specific volume is

$$0.001004(1000) = 1.004 \text{ m}^3/\text{kg}$$

At 200 kPa, you interpolate between 400 K, at which $V = 0.9024 \text{ m}^3/\text{kg}$, and 450 K, at which $V = 1.025 \text{ m}^3/\text{kg}$, which range covers the specific volume of 1.004 m³/kg. You find T by solving the linear interpolation relation

$$0.9024 \frac{\text{m}^3}{\text{kg}} + \frac{(1.025 - 0.9024) \text{m}^3/\text{kg}}{(450 - 400) \text{K}} (T - 400) \text{K} = 1.004 \frac{\text{m}^3}{\text{kg}}$$

$$T = 4300 + 41 = 441 \text{ K}$$

You have probably often heard of the saying: a picture is worth a 1000 words. Something similar might be said of two-dimensional charts, namely that you can get an excellent idea of the values of the enthalpy and other properties of a substance in all of the regions displayed in a chart. Although the accuracy of the values read from a chart may be limited (depending on the scale of the chart), tracing out various

processes on a chart enables you to rapidly visualize and analyze what is taking place. Charts are certainly a simple and quick method for you to get data to compute enthalpy changes. Figure 23.6 for n-butane is an example chart. A number of sources of charts are listed in the references at the end of the chapter. Appendix J contains charts for toluene and carbon dioxide. The CD that accompanies this book also has p - H charts that can be expanded to read property values more accurately. A search of the Internet will turn up additional charts.

Charts are drawn with various coordinates, such as p versus \hat{H} , p versus \hat{V} , or p versus T . Since a chart has only two dimensions, the coordinates can represent only two variables. The other variables of interest have to be plotted as lines of constant value across the face of the chart. Recall, for example, that in the p - \hat{V} diagram for CO_2 , Figure 16.4, lines of constant temperature were shown as parameters. Similarly, on a chart with pressure and enthalpy as the axes, lines of constant specific volume and/or temperature might be drawn as in Figure 23.6. This situation limits

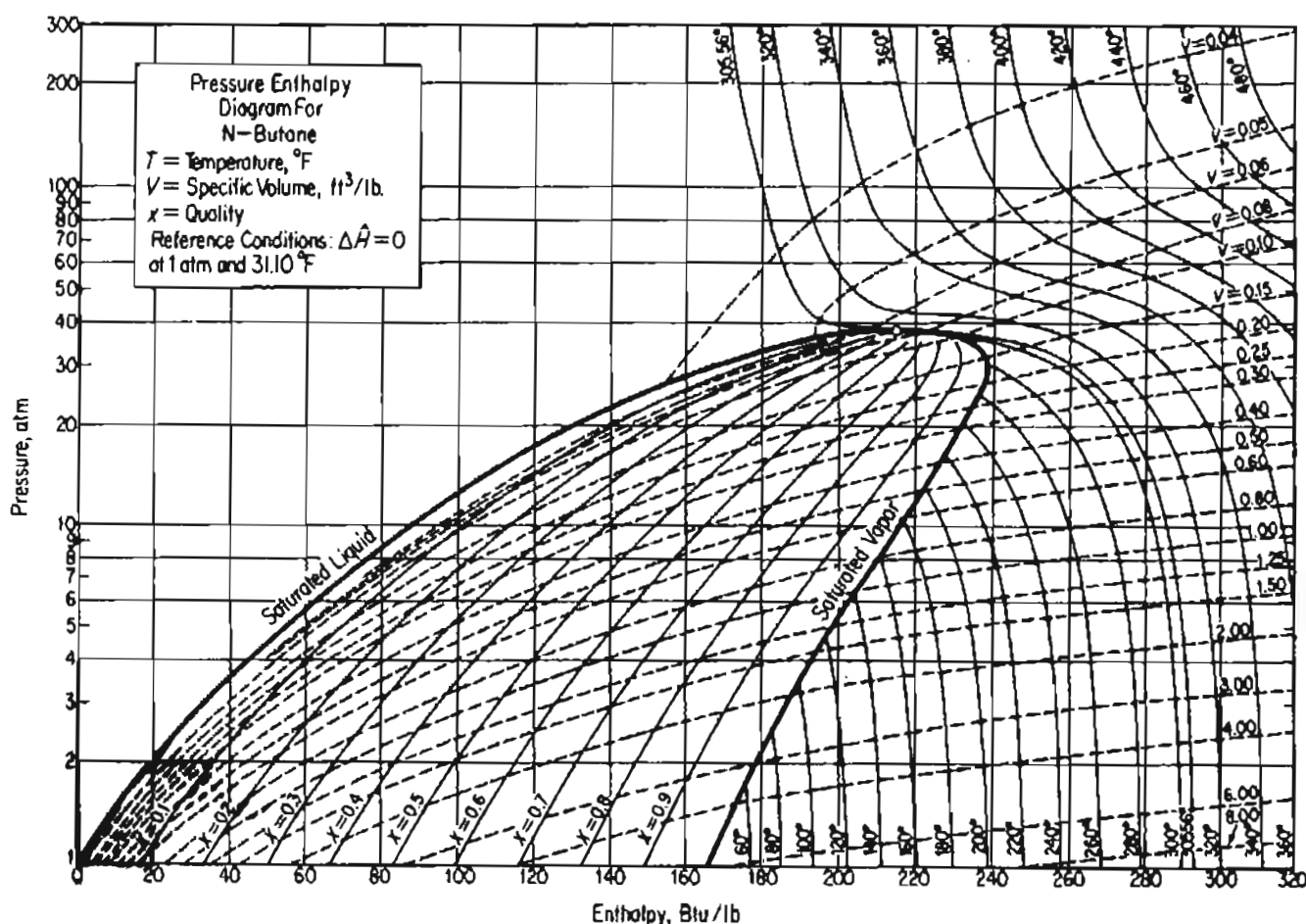


Figure 23.6 Pressure-enthalpy diagram for n-butane. The dashed lines are contours of specific volume, and the solid lines marked with temperatures in °F are lines of constant temperature.

the number of variables that can be presented vis-à-vis tables. How many properties have to be specified for a pure component gas to definitely fix the state of the gas? If you specify two intensive properties for a pure gas, you will ensure that all the other intensive properties will have definite values, and any two intensive properties can be chosen at will. Since a particular state for a gas can be specified by any two independent intensive properties, specifying any two properties on a two-dimensional chart fixes a point at which all the other intensive properties can be read.

EXAMPLE 23.9 Use of the Pressure-Enthalpy Chart for Butane to Calculate the Enthalpy Difference between Two States

Calculate $\Delta \hat{H}$, $\Delta \hat{V}$, and ΔT changes for 1 lb of saturated vapor of *n*-butane going from 2 atm to 20 atm (saturated).

Solution

Obtain the necessary data from Figure 23.6

	\hat{H} (Btu/lb)	\hat{V} (ft ³ /lb)	T (°F)
Saturated vapor at 2 atm:	179	3.00	72
Saturated vapor at 20 atm:	233	0.30	239

$$\Delta \hat{H} = 233 - 179 = 54 \text{ Btu/lb}$$

$$\Delta \hat{V} = 0.30 - 3.00 = -2.70 \text{ ft}^3/\text{lb}$$

$$\Delta T = 239 - 72 = 167^\circ\text{F}$$

SELF-ASSESSMENT TEST

Questions

1. Explain how you would calculate $\Delta \hat{H}$ for a substance that changes from one state to another if you have to use two different tables to cover the range of the change and the reference states for the tables differ.
2. What is the reference state for water in the SI steam tables? In the American Engineering steam tables? Are they the same states?
3. At 250°F and 50 psia, what is \hat{H} for water?

Problems

1. What is the enthalpy change needed to change 3 lbs of liquid water at 32°F to steam at 1 atm and 300°F?

2. What is the enthalpy change needed to heat 3 lbs of water from 60 psia and 32°F to steam at 1 atm and 300°F?
3. What is the enthalpy change needed to change 1 lb of a water–steam mixture of 60% quality to one of 80% quality if the mixture is at 300°F?
4. What is the enthalpy change that occurs when 1 kg of water goes from 200 kPa and 600 K to 1000 kPa and 400 K? Repeat for the internal energy.
5. Calculate $\Delta \hat{H}$ for 1 g mol of NO_2 gas that changes temperature from 300 K to 1000 K.
6. Calculate the enthalpy change that occurs when 1 lb of CO_2 changes state from 8 psia and a mixture containing 20% liquid plus saturated solid to 200°F by a constant volume process. Hint: Look at the CO_2 chart in the Appendix.

Discussion Problem

1. How would you go about preparing an enthalpy versus pressure chart for ethylene? List the types of data needed to make the calculations, and specify the equations that you would use.

23.4 Computer Databases

*Numbers have souls, and you
Can't help but get involved
With them in a personal way.*

Paul Auster, *The Music of Chance*

Values of the properties of thousands of substances are available via software programs that can provide sets of values of physical properties at any given state. Thus you avoid the need for interpolation and/or auxiliary computation, such as problems in which ΔU must be calculated from $\Delta U = \Delta H - \Delta(pV)$. One such program is included on the CD that accompanies this book. The program is abridged so that it does not have the accuracy nor cover the range of commercially available programs, but it is quite suitable for solving problems in this text. Professor Yaws has been kind enough to provide the data for most of the 750 compounds. If you want to save time in your calculations, be sure to examine the CD that accompanies this book to ascertain the types of properties available to you. Instructions for the use of the CD are in the back of the book.

You can also purchase comprehensive databases, and design packages that contain different ways to calculate the properties of a large number of compounds. You can get immediate access to many free information systems via the Internet. At the end of the chapter is a list of a number of such sources of information.

SELF-ASSESSMENT TEST

Questions

1. Where can you find sources on the Internet that provide free data for steam properties?
2. How are values in tables of properties calculated? State what kinds of experimental values must be collected to obtain \hat{H} , \hat{U} , and \hat{V} .

Problems

Use the CD in the back of this book or Internet sites in solving the problems below.

1. Calculate the enthalpy change in 24 g of N_2 if heated from 300 K to 1500 K at constant pressure.
2. What is the enthalpy change when 2 lb of *n*-butane gas is cooled from 320°F and 2 atm to saturated vapor at 6 atm?
3. You are told that 4.3 kg of water at 200 kPa occupies (a) 4.3, (b) 43, (c) 430, (d) 4300, and (e) 43,000 liters. State for each case whether the water is in the solid, liquid, liquid–vapor, or vapor regions.
4. Water at 400 kPa and 500 K is cooled to 200 kPa and 400 K. What is the enthalpy change?
5. Calculate the enthalpy change when 1 lb of benzene is changed from a vapor at 300°F and 1 atm to a solid at 0°F and 1 atm.

Looking Back

In this chapter we described common ways in which values of the enthalpy for pure substances can be retrieved via heats of transition, heat capacity equations, tables, charts, and databases.

GLOSSARY OF NEW WORDS

Clapeyron equation An exact thermodynamic equation that relates the slope of the vapor–pressure curve and the molar heat of vaporization.

Clausius-Clapeyron equation An integrated version of the Clapeyron equation for constant heat of vaporization.

Heat capacity The change of internal energy or the change of enthalpy with respect to temperature.

Heat of condensation The negative of the heat of vaporization.

Heat of fusion The enthalpy change for the phase transition of melting.

Heat of solidification The negative of the heat of fusion.

Heat of sublimation The enthalpy change of a solid directly to vapor.

Heat of vaporization The enthalpy changes for the phase transition of a liquid to a vapor.

Latent heat An enthalpy change that involves a phase transition.

Phase transitions A change from the solid to the liquid phase, from the liquid to the gas phase, from the solid to the gas phase, or the respective reverse changes.

Reference substance plots Plots used to estimate values of physical properties based on comparison with the same properties of a substance used as a reference.

Sensible heat An enthalpy change that does not involve a phase transition.

SUPPLEMENTARY REFERENCES

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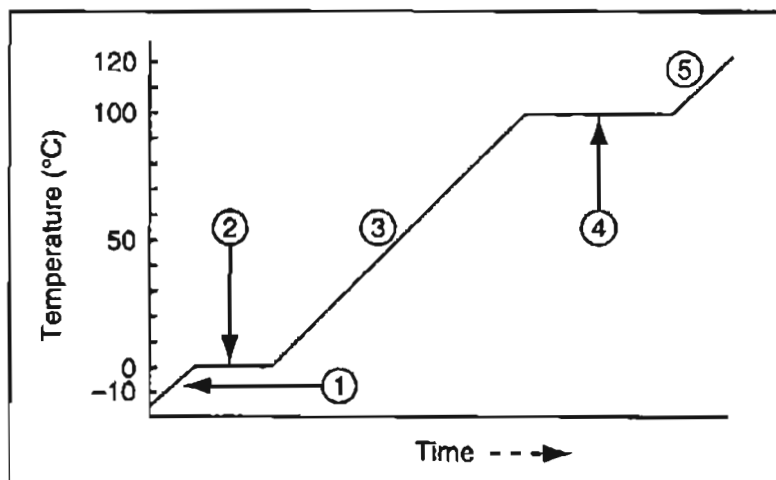
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PROBLEMS

- *23.1 Which is an example of an exothermic phase change? (1) liquid to solid; (2) liquid to gas; (3) solid to liquid; (4) solid to gas.
- *23.2 Explain the difference between latent heat and sensible heat, and compare their relative magnitudes.
- *23.3 Does the heat of vaporization depend on temperature?
- *23.4 Heat is added to a substance at a constant rate and the temperature of the substance remains the same. This substance is (1) solid melting at its melting point; (2) solid below its melting point; (3) liquid above its freezing point; (4) liquid freezing at its freezing point.

- *23.5 The graph below shows a pure substance which is heated by a constant source of heat supply.



Use the numbers in the diagram to denote the following stages:

- (a) being warmed as a solid
- (b) being warmed as a liquid
- (c) being warmed as a gas
- (d) changing from a solid to a liquid
- (e) changing from a liquid to a gas

Also, what is its boiling temperature? The freezing temperature?

- *23.6 Show that the heat (enthalpy) of fusion is essentially identical to the internal energy of fusion.
- *23.7 The vapor pressure of zinc in the range 600 to 985°C is given by the equation

$$\log_{10} p = -\frac{6160}{T} + 8.10$$

where p = vapor pressure, mm Hg

T = temperature, K

Estimate the latent heat of vaporization of zinc at its normal boiling point of 907°C.

- *23.8 The vapor pressure of phenylhydrazine has been found to be (from 25° to 240°C):

$$\log_{10} p^* = 7.9046 - \frac{2366.4}{T + 230}$$

where p^* is in atm and T is in °C. What is the heat of vaporization of phenylhydrazine in Btu/lb mol at 200°F?

Use the Clausius-Clapeyron equation.

- **23.9 Use the Clausius-Clapeyron equation to solve the following problem. One hundred g mol of benzene (C_6H_6) are placed in a 100 L vessel at 35°C. What is the vapor pres-

sure of benzene at 35°C? Data: At 320 K the vapor pressure of benzene is measured and found to be 0.2111 atm, and the physical property data at 320 K (from a hand-book) are:

$\frac{\Delta \hat{H}_{\text{Liquid}} (\text{J/g})}{423.8}$	$\frac{\Delta \hat{H}_{\text{vapor}} (\text{J/g})}{841.5}$	$\frac{\hat{V}_{\text{Liquid}} (\text{cm}^3/\text{g})}{1.133 \times 10^{-3}}$	$\frac{\hat{V}_{\text{vapor}} (\text{cm}^3/\text{g})}{1.046}$
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- *23.10** Estimate ΔH_v for n-heptane at its normal boiling point given: $T_b = 98.43^\circ\text{C}$, $T_c = 540.2 \text{ K}$, $p_c = 27 \text{ atm}$. Use Chen's Equation. Calculate the % error in this value compared to the tabulated value of 31.69 kJ/g mol.
- **23.11** Determine the heat of vaporization of benzene at its normal boiling point by using Riedel's equation (Equation 23.6).
- *23.12** Cumene, C_9H_{12} , (isopropyl benzene) has a normal boiling point of 152.4°C . Estimate the heat of vaporization of cumene at 100°C using the Watson equation.
- ***23.13** Estimate each of the following:
- Heat of sublimation of ice
 - Heat of vaporization of water
 - Heat of fusion of ice
 - The triple point of water
- Using the equations in section 23.1.
- ***23.14** Some measurements of the thermodynamic properties of n-butane gave the following values at 30°C :
- Specific gravity of saturated liquid = 0.564 g/cm^3
 Specific gravity of saturated vapor (air = 1.00 at 0°C and 1 atm) = 6.50
 Latent heat of vaporization = 356.5 J/g
 The vapor pressure as a function of temperature (T in K) was found to be

$$\log_{10}(p \text{ atm}) = 1.767 - \frac{1,337}{T} + 1.75 \log_{10} T - 0.004T$$

As an embryonic engineer, you are asked to evaluate the above data, and determine whether or not the values are consistent.

- *23.15** An oil, with a density less than one, and containing small quantities of water, was being heated in a vessel in order to drive off the water vapour, prior to carrying out a reaction. The water and oil were immiscible.

The heating medium was a heat transfer fluid at 250°C , the heat being transmitted *via* concentric coils, the fluid being in the coils.

During the initial stages the manhole was partly open and, after heating had been applied for some time the operator noticed that he had omitted to start the agitator. On doing this large quantities of the oil were ejected with considerable force through the open manhole and ejection continued until only approximately one quarter of the original contents were left in the reactor.

What was the cause of this accident?

- *23.16 Estimate the heat capacity of gaseous isobutane at 1000 K and 200 mm Hg by using the Kothari-Doraiswamy relation

$$C_p = A + B \log_{10} T_r$$

from the following experimental data at 200 mm Hg:

$C_p[\text{J}/(\text{K})(\text{g mol})]$	97.3	149.0
Temperature(K)	300	500

The experimental value is 227.6; what is the percentage error in the estimate?

- *23.17 Heat capacity data for gaseous NH_3 are listed below:

$T(^{\circ}\text{C})$	$\text{J}/(\text{g mol})(^{\circ}\text{C})$
0	35.02
100	37.80
200	41.10
300	44.60
400	47.48
500	50.40
600	53.14
700	55.69
800	58.06
900	60.24
1000	62.63
1100	64.04
1200	65.66

Fit an equation of the form $C_p = a + bT + cT^2$ and an equation of the form $C_p = a + bT + cT^2 + dT^3$. Compare your results with the heat capacity equation for NH_3 gas in Appendix E. Hint: Use Polymath.

- *23.18 Experimental values calculated for the heat capacity of ammonia from -40 to 1200°C are:

$T(^{\circ}\text{C})$	C_p [cal/(g mol)($^{\circ}\text{C}$)]	$T(^{\circ}\text{C})$	C_p [cal/(g mol)($^{\circ}\text{C}$)]
-40	8.180	500	12.045
-20	8.268	600	12.700
0	8.371	700	13.310
18	8.472	800	13.876
25	8.514	900	14.397
100	9.035	1000	14.874
200	9.824	1100	15.306
300	10.606	1200	15.694
400	11.347		

Fit the data by least squares for the following two functions:

$$\left. \begin{aligned} C_p^0 &= a + bT + cT^2 \\ C_p^0 &= a + bT + cT^2 + dT^3 \end{aligned} \right\} \text{ where } T \text{ is in } ^\circ\text{C}$$

Hint: Use Polymath.

- *23.19** Experimental values of the heat capacity C_p have been determined in the laboratory as follows; fit a second-order polynomial in temperature to the data ($C_p = a + bT + cT^2$):

$T(^{\circ}\text{C})$	$C_p [\text{J}/(\text{g mol})(^{\circ}\text{C})]$
100	40.54
200	43.81
300	46.99
400	49.33
500	51.25
600	52.84
700	54.14

(The data are for carbon dioxide.)

- *23.20** An equation for the heat capacity of acetone vapor is

$$C_p = 71.96 + 20.10 \times 10^{-2} T - 12.78 \times 10^{-5} T^2 + 34.76 \times 10^{-9} T^3$$

where C_p is in $\text{J}/(\text{g mol})(^{\circ}\text{C})$ and T is in $^{\circ}\text{C}$. Convert the equation so that C_p is in $\text{Btu}/(\text{lb mol})(^{\circ}\text{F})$ and T is in $^{\circ}\text{F}$.

- *23.21** Your assistant has developed the following equation to represent the heat capacity of air (with C_p in $\text{cal}/(\text{g mol})(\text{K})$ and T in K):

$$C_p = 6.39 + 1.76 \times 10^{-3} T - 0.26 \times 10^{-6} T^2$$

- Derive an equation giving C_p but with the temperature expressed in $^{\circ}\text{C}$.
- Derive an equation giving C_p in terms of Btu per pound per degree Fahrenheit with the temperature being expressed in degrees Fahrenheit.

- *23.22** An equation for the heat capacity of carbon (solid) was given in an article as

$$C_p = 1.2 + 0.0050 T - 0.0000021 T^2$$

where C_p is in $\text{Btu}/(\text{lb})(^{\circ}\text{F})$ and T is in $^{\circ}\text{F}$. The calculated value of the enthalpy for C at 1000°F is $1510 \text{ Btu}/\text{lb}$. What is the reference temperature for the calculation of the enthalpy of carbon?

- *23.23** You have been asked to review the calculations of an assistant with respect to the calculation of the internal energy of CO_2 . The assistant looked up the enthalpy of CO_2 at 600 kPa and 283K ($16,660 \text{ kJ}/\text{gmol}$), and then calculated on the basis of 1 g mol

$$p\hat{V} = zRT \quad \text{so } \hat{U} = \hat{H} - p\hat{V} = H - zRT$$

$$\hat{U} = 16,660 - \frac{0.96}{1} \left| \frac{8.314}{1} \right| \left| \frac{283}{1000} \right| = 16,658$$

Is this calculation correct?

- *23.24 The enthalpy of Al_2O_3 can be represented by the equation

$$\hat{H}(T) - \hat{H}(273) = 92.38T + 1.877 \times 10^{-2} T^2 + \frac{2.186 \times 10^6}{T} - 34,635$$

where ΔH is in J/g mol and T is in K. Determine an equation for the heat capacity of Al_2O_3 as a function of temperature.

- **23.25 G. E. Moore reported an equation for the high temperature enthalpy of manganese dioxide as:

$$\hat{H}(T) - \hat{H}(298) = 16.60 T + 1.22 \times 10^{-3} T^2 - \frac{388,000}{T} - 6360$$

Is this equation valid?

- *23.26 General Electric Co. has developed an advanced fuel-cell battery that will supply the primary power needed during orbit by space capsules. The peak load delivered by the battery will be just under 2 kW. The facility will be assembled from ion-exchange-membrane cells, in which the membranes are sheets of a tough, undisclosed plastic.

The fuels supplied to the cells will be hydrogen and oxygen. Though fed in the gaseous state during battery operation, these two elements will be stored as liquids, to conserve space.

The equipment is inherently reliable because it is simple, and it achieves 60% thermal efficiency under normal load. Also, the battery will yield a by-product that is highly valuable in space-flight—a pint of pure drinkable water for each kilowatt-hour of operation.

If the O_2 and the H_2 are stored as saturated liquids at their normal boiling point, what is the enthalpy change per g mol of O_2 between the liquid storage tank and the state at which the O_2 enters the fuel cell (1.5 atm, 27 °C).

- *23.27 Two gram moles of nitrogen are heated from 50°C to 250°C in a cylinder. What is ΔH for the process? The heat capacity equation is

$$C_p = 27.32 + 0.6226 \times 10^{-2} T - 0.0950 \times 10^{-5} T^2$$

where T is in kelvin and C_p is in J/(g mol)(°C).

- *23.28 Calculate the change in enthalpy for 5 kg mol of CO which is cooled from 927°C to 327°C.
- *23.29 Hydrogen sulfide is heated from 77°C to 227°C. What is the enthalpy change due to the heating?
- *23.30 What is the enthalpy change for acetylene when heated from 37.8°C to 93.3°C?

- *23.31** You are asked to calculate the electric power required (in kWh) to heat all of an aluminum wire (positioned in a vacuum similar to a light bulb filament) from 25°C to 660°C (liquid) to be used in a vapor deposition apparatus. The melting point of Al is 660°C. The wire is 2.5 mm in diameter and has a length of 5.5 cm. (The vapor deposition occurs at temperatures in the vicinity of 900°C).

Data: For Al, $C_p = 20.0 + 0.0135 T$ where T is in K and C_p is in $J/(g \text{ mol})(^\circ C)$. The $\Delta H_{\text{fusion}} = 10,670 J/(g \text{ mol})(^\circ C)$ at 660°C. The density of Al is 19.35 g/cm^3 .

- *23.32** Calculate the enthalpy change (in J/kg mol) that takes place in raising the temperature of 1 kg mol of the following gas mixture from 50°C to 550°C.

Component	Mol %
CH ₄	80
C ₂ H ₆	20

- **23.33** In a proposed molten-iron coal gasification process (*Chemical Engineering*, July 1985: 17), pulverized coal of up to 3 mm size is blown into a molten iron bath, and oxygen and steam are blown in from the bottom of the vessel. Materials such as lime for settling the slag, or steam for batch cooling and hydrogen generation, can be injected at the same time. The sulfur in the coal reacts with lime to form calcium sulfide, which dissolves into the slag. The process operates at atmospheric pressure and 1400 to 1500°C. Under these conditions, coal volatiles escape immediately and are cracked. The carbon conversion rate is said to be above 98%, and the gas is typically 65 to 70% CO, 25 to 35% H₂, and less than 2% CO₂. Sulfur content of the gas is less than 20 ppm.

Assume that the product gas is 68% CO, 30% H₂, and 2% CO₂, and calculate the enthalpy change that occurs on the cooling of 1000 m³ at 1400°C and 1 atm of gaseous product from 1400°C to 25°C and 1 atm. Use the table for the enthalpies of the combustion gases.

- **23.34** Determine the enthalpy change when one gram mole of SO₂ gas is cooled from 538°C to -101°C at 1 atmosphere pressure. *Data:*

Boiling point:	-5°C
Melting point:	-75.5°C
Latent heat of vaporization:	24,940 J/g mol
Latent heat of fusion:	7,401 J/g mol
Use the average C_p of liquid SO ₂ as:	1.28 J/(g mol)(°C)
Use the average C_p of solid SO ₂ as:	0.958 J/(g mol)(°C)
Use the C_p of gaseous SO ₂ from Appendix E.	

- **23.35** Calculate the enthalpy change (in joules) that occurs when 1 kg of benzene vapor at 150°C and 100 kPa condenses to a solid at -20.0°C and 100 kPa.
- **23.36** One hundred kg of HCl gas are cooled from 300 to 150°C at 1 atm pressure. Calculate ΔH and ΔU in kJ. The heat capacity equation found in a handbook is

$$C_p = 7.24 - 1.76 \times 10^{-3}T + 3.07 \times 10^{-6}T^2 - 10^{-9}T^3$$

where C_p is in $\frac{\text{kg cal}}{(\text{kg mol})(\text{K})}$ and T is in K .

***23.37** Use the tables for the heat capacities of the combustion gases in the Appendix to compute the enthalpy change (in Btu) that takes place when a mixture of 6.00 lb mol of gaseous H_2O and 4.00 lb mol of CO_2 is heated from 60°F to 600°F .

✓ ****23.38** Use of the steam tables:

- What is the enthalpy change needed to change 3 lb of liquid water at 32°F to steam at 1 atm and 300°F ?
- What is the enthalpy change needed to heat 3 lb of water from 60 psia and 32°F to steam at 1 atm and 300°F ?
- What is the enthalpy change needed to heat 1 lb of water at 60 psia and 40°F to steam at 300°F and 60 psia?
- What is the enthalpy change needed to change 1 lb of a water-steam mixture of 60% quality to one of 80% quality if the mixture is at 300°F ?
- Calculate the ΔH value for an isobaric (constant pressure) change of steam from 120 psia and 500°F to saturated liquid.
- Repeat part (e) for an isothermal change to saturated liquid.
- Does an enthalpy change from saturated vapor at 450°F to 210°F and 7 psia represent an enthalpy increase or decrease? A volume increase or decrease?
- In what state is water at 40 psia and 267.24°F ? At 70 psia and 302°F ? At 70 psia and 304°F ?
- A 2.5-ft³ tank of water at 160 psia and 363.5°F has how many cubic feet of liquid water in it? Assume that you start with 1 lb of H_2O . Could it contain 5 lb of H_2O under these conditions?
- What is the volume change when 2 lb of H_2O at 1000 psia and 20°F expands to 245 psia and 460°F ?
- Ten pounds of wet steam at 100 psia has an enthalpy of 9000 Btu. Find the quality of the wet steam.

***23.39** Use the steam tables to calculate the enthalpy change (in joules) of 2 kg mol of steam when heated from 400 K and 100 kPa to 900 K and 100 kPa. Repeat using the table in the text for the enthalpies of combustion gases. Repeat using the heat capacity for steam. Compare your answers. Which is most accurate?

***23.40** A closed vessel contains steam at 1000.0 psia in a 4- to-1 vapor volume-to-liquid volume ratio. What is the steam quality?

***23.41** What is the enthalpy change in British thermal units when 1 gal of water is heated from 60°F to 1150°F and 240 psig.

***23.42** What is the enthalpy change that takes place when 3 kg of water at 101.3 kPa and 300 K are vaporized to 15,000 kPa and 800K?

✓ ****23.43** Wet steam flows in a pipe at a pressure of 700 kPa. To check the quality, the wet steam is expanded adiabatically to a pressure of 100 kPa in a separate pipe. A thermo-couple inserted into the pipe indicates the expanded steam has a temperature of 125°C . What was the quality of the wet steam in the pipe prior to expansion?

- *23.44 If 30 m³ of combustion products at 1100K of the following composition: 6.2% O₂, 1.0% H₂O, 12.3% CO₂, and the balance N₂ are cooled at atmospheric pressure from 1100 K to 300 K, what is the enthalpy change in kJ? Use the table for the enthalpies of the combustion gases.
- *23.45 Equal quantities by weight of water at +50°C and of ice at -40°C are mixed together. What will be the final temperature of the mixture?
- *23.46 A chart for carbon dioxide (see Appendix) shows that the enthalpy of saturated CO₂ liquid is zero at -40°F. Can this be true? Explain your answer.
- *23.47 Use the CO₂ chart for the following calculations.
- (a) Four pounds of CO₂ are heated from saturated liquid at 20°F to 600 psia and 180°F.
 - (1) What is the specific volume of the CO₂ at the final state?
 - (2) Is the CO₂ in the final state gas, liquid, solid, or a mixture of two or three phases?
 - (b) The 4 lb of CO₂ is then cooled at 600 psia until the specific volume is 0.07 ft³/lb.
 - (1) What is the temperature of the final state?
 - (2) Is the CO₂ in the final state gas, liquid, solid, or a mixture of two or three phases?
- *23.48 Calculate the internal energy (actually $\Delta \hat{U}$) of CO₂ at 40°F and 40 psia in Btu/lb. You can use the CO₂ chart in the Appendix of the book for the data.
- *23.49 Calculate the enthalpy change in heating 1 g mole of CO₂ from 50° to 100°C at 1 atm. Do this problem by three different methods:
1. Use the heat capacity equation from the Appendix;
 2. Use the CO₂ chart in the Appendix;
 3. Use the Table of Combustion Gases.
- **23.50 Use the chart for n-butane to calculate the enthalpy change for 10 lb of butane going from a volume of 2.5 ft³ at 360°F to saturated liquid at 10 atm.
- **23.51 A propane gas tank is filled, closed and attached to a barbecue grill. After standing some time what is the state of the propane inside the tank? What are the temperature and pressure inside the tank? After using 80% of the propane in the tank, what is the pressure inside the tank after it reaches equilibrium.

CHAPTER 24

APPLICATIONS OF ENERGY BALANCES IN THE ABSENCE OF CHEMICAL REACTIONS

24.1 Simplifications of the General Energy Balance	718
24.2 The Strategy for Solving Energy Balance Problems	723
24.3 Application of the Energy Balance to Closed Systems	728
24.4 Application of the Energy Balance to Open Systems	735

Your objectives in studying this chapter are to be able to:

1. Express the general energy balance in words and write it down with symbols and variables for both open and closed systems.
2. Simplify the energy balance equation in conformity with the problem statement and other information.
3. Apply simplified energy balances to solve specific problems involving both open and closed systems.

Although we have discussed energy balances in Chapter 22, to this point you have only been exposed to very simple processes so that we could present the concepts involved without excessive details. Now it's time to dig into more complex problems so that you can apply all of the principles discussed in the last three chapters.

Looking Ahead

In this section we apply the general energy balance in the absence of chemical reaction, Equation (22.7), to closed and open systems without reaction. Material balances will be combined with energy balances in the examples at the end of the chapter.

24.1 Simplifications of the General Energy Balance

Going only part of the way is not the same as going the wrong way.

Jostein Gaarden, *Sophie's World*

Given the problem statement, and often implied but not stated constraints, you can simplify the general energy balance developed in Chapter 22. We reproduce it here using concise symbols as in Equation (22.6) with “inside” and “flow” appended to refresh your memory about the system. “Inside” refers to the system inside the system boundary while “flow” refers to streams that cross the system boundary.

$$\begin{aligned}\Delta E_{\text{inside}} &\equiv \Delta(U + PE + KE)_{\text{inside}} = Q + W - \Delta(H + PE + KE)_{\text{flow}} \\ &= Q + W - \Delta[m(\hat{H} + \hat{PE} + \hat{KE})]\end{aligned}\quad (24.1)$$

In most problems you do not have to use all of the terms of the general energy balance equation. Certain terms may by implication or judgment be zero or may be so small that they can be neglected in comparison with the other terms. Other terms may be stated to be small or zero. As a result, when you apply Equation (24.1) to processes, you need to consider only certain terms in the equation. The three most commonly used applications of Equation (24.1) are to:

1. closed systems
2. open systems with heat transfer into and out of the process
3. open, steady-state flow systems.

What follows is an analysis of each of these cases along with some physical examples:

1. **Closed system.** For closed or **batch systems**, no mass flow occurs in or out of the system ($m_1 = m_2 = 0$) so that:

$$\Delta E = Q + W \quad (24.2)$$

If there is no accumulation ($\Delta E = 0$),

$$Q = -W \quad (24.3)$$

An example is the initial heating to expand a hot air balloon.

2. **Open system with heat transfer.** Many open, steady-state processes in the chemical processing industries exist, processes that are dominated by heat transfer, Q . For these cases, ΔE , W , ΔPE , and ΔKE can be neglected because they are small compared to Q and ΔH or are zero. For these cases, Equation (24.1) reduces to

$$Q = \Delta[m\hat{H}] = \Delta H \quad (24.4)$$

Equation (24.4) can be applied to heat exchangers (i.e., devices for transferring heat from a high temperature fluid to a lower temperature fluid) and distillation columns.

If no heat transfer takes place between the system and the surroundings, Equation (24.4) reduces to

$$\Delta H = 0 \quad (24.5)$$

Equation (24.5) is sometimes called the “**enthalpy balance**,” and is used to model the mixing of two fluids at different temperatures.

A particularly tragic example of an open, unsteady-state system occurred on April 12, 1963, when the submarine *Thresher* on a test dive at its maximum depth (1300 ft) sank off the coast of Cape Cod with 129 men aboard. A silver brazed pipe connection through the exterior surface of the submarine failed, and ocean water poured into the vessel. The commander ordered that the ballast tanks be blown so that the vessel could surface, but the air in the high-pressure reservoirs at 4500 psia contained water vapor, and on expansion into the ballast tanks the air temperature dropped much so that the water vapor froze, blocking the pipelines to the ballast tanks within 90 seconds.

3. **Open, steady-state flow system.** For steady-state ($\Delta E = 0$) flow systems that do not involve significant heat transfer ($Q = 0$), Equation (24.1) reduces to

$$W = \Delta PE + \Delta KE \quad (24.6)$$

You can use Equation (24.6) to size pumps or calculate the pressure drop through a piping network.

In addition to the three types of processes listed above, other processes require the use of all of the terms in Equation (24.1). Sometimes both Q and ΔKE are simultaneously significant. In addition, you can also reach certain conclusions by inference from the nature of the material in the process and its

conditions. For example, for solids or liquids at constant temperature, $\Delta\hat{U} \cong 0$. Similarly, for a near ideal isothermal gas, $\Delta\hat{U} \cong 0$ and $\Delta\hat{H} \cong 0$.

Some special process names associated with energy balance problems that we have mentioned in previous chapters are worth remembering:

- a. *Isothermal* ($dT = 0$): constant temperature process
- b. *Isobaric* ($dp = 0$): constant pressure process
- c. *Isometric or isochoric* ($dV = 0$): constant volume process
- d. *Adiabatic* ($Q = 0$): no heat interchange. If we inquire as to the circumstances under which a process can be called adiabatic, one of the following is most likely:
 - (1) the system is insulated.
 - (2) Q is very small in relation to the other terms in the energy equation and may be neglected.
 - (3) the process takes place so fast that there is no time for heat to be transferred.

EXAMPLE 24.1 Simplification of the General Energy Balance

Figure E24.1 illustrates a process in which several segments are distinguished by numbered boundaries. List the simplifying assumptions to make in Equation (24.1) for the following segments: 1 to 5, 4 to 5, 3 to 4, 3 to 5, and 1 to 3.

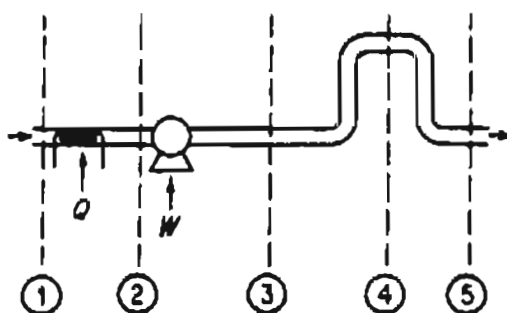


Figure E24.1

Here is the analysis for each segment

- 1 to 5: • $\Delta\hat{P}\hat{E} = 0$ (no level change)
- Probably $\Delta\hat{K}\hat{E} = 0$
 - $\Delta\hat{E} = 0$ (process appears to be steady state)
- Result: $\hat{Q} + \hat{W} = \Delta\hat{H}$

$$4 \text{ to } 5: \bullet \hat{Q} = \hat{W} = 0$$

$$\bullet \Delta \widehat{KE} \cong 0$$

$$\bullet \Delta \hat{E} = 0$$

$$\text{Result: } \Delta \hat{H} = -\Delta \widehat{PE}$$

$$3 \text{ to } 4: \bullet \hat{Q} = \hat{W} = 0$$

$$\bullet \Delta \widehat{KE} \cong 0$$

$$\bullet \Delta \hat{E} = 0$$

$$\text{Result: } \Delta \hat{H} = -\Delta \widehat{PE}$$

$$3 \text{ to } 5: \bullet \hat{Q} = \hat{W} = 0$$

$$\bullet \Delta \widehat{PE} = 0$$

$$\bullet \Delta \widehat{KE} \cong 0$$

$$\bullet \Delta \hat{E} = 0$$

$$\text{Result: } \Delta \hat{H} = 0$$

$$1 \text{ to } 3: \bullet \Delta \widehat{PE} = 0$$

$$\bullet \Delta \widehat{KE} \text{ may be approximately } 0$$

$$\bullet \Delta \hat{E} = 0$$

$$\text{Result: } \hat{Q} + \hat{W} = \Delta \hat{H}$$

SELF-ASSESSMENT TEST

Questions

- Answer the following questions true or false:
 - In an open system ΔE is always zero.
 - In a closed system ΔE is never zero.
- Can the enthalpy change between two locations in an open flow system be zero even if work and/or heat is done on or by the system? Explain your answer.

Problems

- Simplify Equation (24.1) as much as possible for sections (a) 2 to 3 and (b) 2 to 4 in Figure E24.1
- A laboratory cylinder is opened and N_2 gas flows out. If the system is the cylinder, simplify the general energy balance as much as you reasonably can stating all assumptions you make. See Figure SAT24.1P2.

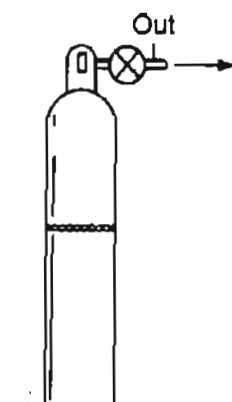


Figure SAT24.1P2

3. Examine the process displayed in Figure SAT24.1P3.

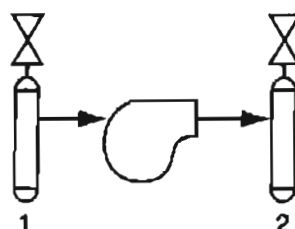


Figure SAT24.1P3

Gas flows steadily (the valves are open) from a high pressure at 1 to low pressure at 2 through a turbine that produces work. Simplify the general energy balance for the system comprised of both cylinders and the turbine, eliminating as many terms as possible.

Thought Problems

1. On which side of a building should the intake for an air compressor be located, and why?
2. Do you save energy if you
 - a. let ice build up inside your freezer?
 - b. use extra laundry detergent?
 - c. light a fire in your conventional fireplace?
 - d. turn off your window air conditioner if you will be gone for a couple of hours?
 - e. take baths rather than showers?
 - f. use long-life incandescent lightbulbs?
 - g. use fluorescent rather than incandescent lights?
 - h. install your refrigerator beside your range?
 - i. drive 55 instead of 70 miles per hour?
 - j. choose a car with air conditioning, power steering, and an automatic transmission over one without these features?

24.2 The Strategy for Solving Energy Balance Problems

*... he who seeks for methods without having a
definite problem in mind seeks for the most part in vain.*

David Hilbert

In Chapter 8 you read about the strategy for solving material balance problems. In this section we augment the problem-solving strategy with suggestions on how to incorporate energy balances. We assume that the steps listed in Chapter 8 will be used along with the following additional recommendations.

*"When a sailor doesn't know what harbor
he is making for," counseled the Roman
philosopher Seneca, "no wind is the right wind".*

1. Choose the system, identify its boundary, and then decide whether the system is open or closed. Write the decision down. Change it if your first decision proves to be a poor one.
2. Decide if the system is steady state or unsteady state. Write the decision down.
3. Write down the general energy balance, Equation (24.1) or (22.7), for the system (one for each system if you pick multiple systems) along with the other equations.
4. Simplify the general energy balance as much as possible by using information in the problem statement and reasonable assumptions based on your understanding of the process.
5. Carry out a degree-of-freedom analysis that includes the energy balance as one equation (that may include more than one additional variable) along with the material balances.
6. Choose a reference state for your calculations, usually the specification of temperature and pressure, but other variables may be substituted.
7. Based on the reference state, get any needed physical property data (T , p , \hat{V} , \hat{U} , \hat{H}) and add the values of the data to the sketch of the process. Be sure to include phase changes. (We defer until Chapter 28 discussion of mixing effects.)
8. Solve the energy balance alone or in conjunction with the material balances.

When an energy balance is used in solving a problem, keep in mind that the **enthalpy of a stream is an explicit function of the temperature and pressure in the stream**. Consequently, each stream should be characterized by its temperature and pressure as well as the mass or moles (or fractions) of each component. Often just the temperature of a stream is specified, and the value of the pressure is not mentioned. In such circumstances, for a saturated liquid you can assume the value of

the pressure is the vapor pressure of the liquid. For a gas, if you have to, you can fall back on assuming one atmosphere when no better value is known for the pressure. For two phases you probably can assume equilibrium exists in the absence of better information. You have to use these types of assumptions to make the degrees of freedom zero in ill-posed problems.

We can illustrate the degree-of-freedom analysis via a simple problem. Suppose water (W) and sucrose (S) of one concentration are mixed with W and S of another concentration to produce a sucrose solution (P) of a third concentration. Figure 24.1 shows the open, steady-state system, the flows F_i , and the concentrations x_i with the units suppressed.

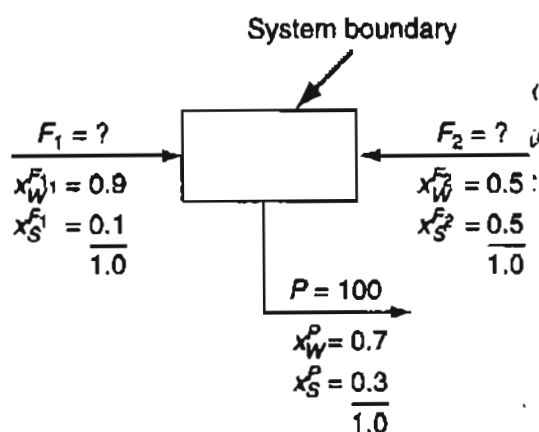


Figure 24.1 Simple mixing process.

The system has 2 unknowns, F_1 and F_2 . To solve for them you can write two independent material balance equations, say

$$\begin{array}{ll} \text{Total} & F_1 + F_2 = 100 \\ \text{Sucrose} & 0.1F_1 + 0.5F_2 = 0.3(100) \end{array}$$

so that the degrees of freedom are zero. You find that $F_1 = F_2 = 50$.

Figure 24.2 (with the units suppressed) shows the same process with the enthalpy values listed for each stream at the respective temperatures and concentrations. Assume that $Q = 0$ so that the energy balance reduces to $\Delta H = 0$.

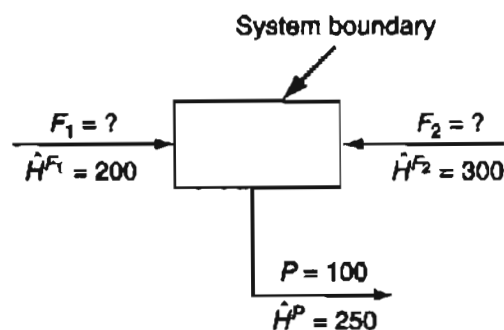


Figure 24.2 Simple mixing process with values of enthalpies given.

Then you can use the energy balance plus the total material balance

$$\begin{array}{ll} \text{Total} & F_1 + F_2 = 100 \\ \text{Energy balance} & 200 F_1 + 300 F_2 = 100 (250) \end{array}$$

to solve for $F_1 = F_2 = 50$. The degrees of freedom again were zero.

Now, suppose the energy balance simplifies to $\Delta H = Q$, and you are asked to solve for Q . We will change \hat{H}^P to be 275 to allow for $Q \neq 0$. Then you would have two independent material balance equations, the ones associated with Figure 24.1, plus one energy balance to solve for three unknowns, F_1 , F_2 , and Q , so that the degrees of freedom are still zero. Solve the material balances first for F_1 and F_2 , and then solve the energy balance for Q

$$\begin{aligned} 100(275) - [200(50) + 300(50)] &= Q \\ Q &= 2500 \end{aligned}$$

The above examples were deliberately made simple to illustrate the concepts involved. In practice, you will encounter cases with zero degrees of freedom in which you must solve the energy and the mass balances simultaneously. You can also encounter cases in which the degrees of freedom are negative or positive, leading to the conclusions outlined in Chapter 8.

*For all its value, the application of a method alone,
is not science, any more than a pile of bricks is
architecture. I would sooner trust a good mind without
a method than a good method without a mind.*

Frank Engler

EXAMPLE 24.2 Degree-of-Freedom Analysis Including an Energy Balance

Figure E24.2 shows a hot gas stream at 500°C being cooled to 300°C by transferring heat to the liquid water that enters at 20°C. You want to find the water flow rate per 100 kg mol of entering hot gas. Carry out a degree-of-freedom analysis for this problem to determine if you can solve it based on the information given above and in Figure E24.2.

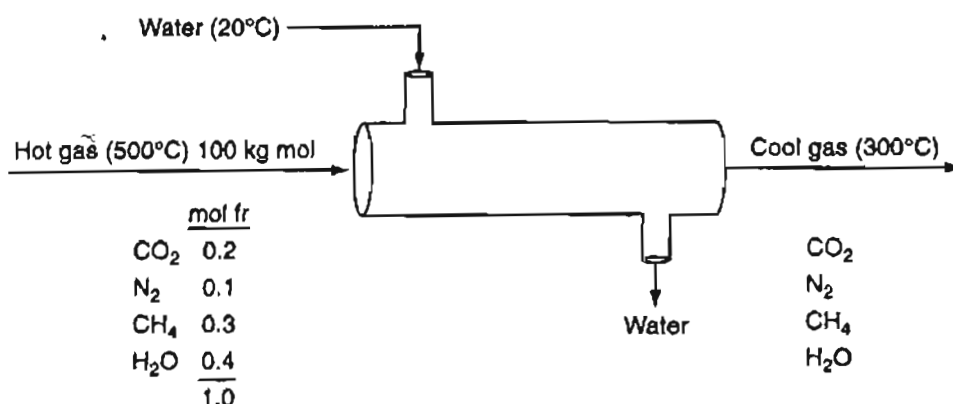


Figure E24.2

Solution

Because $Q = W = 0$ and $\widehat{PE} = \widehat{KE} = 0$ in each stream, with the system being open and steady state, the energy balance reduces to $\Delta H = 0$. Because the problem has 4 components, you can write four independent material balances. Suppose we take the viewpoint that the flow of each component (stream flow) is a variable. Then, considering all of the variables, the problem involves nine stream flow variables (some of which are known, of course), and three temperatures. As for the stream pressures, we have to assume they are specified; implicitly the water will be at its vapor pressure.

Based on the above preliminary analysis, you can form a table to carry out the degree-of-freedom analysis.

Number of variables involved:

Material		
Hot gas:	4 component flows, T , and p	6
Cool gas:	4 component flows, T , and p	6
Water in:	1 component flow, T , and p	3
Water out:	1 component flow, T , and p	3
Energy:		
	Q and W	2
	H , PE , and KE associated with each stream flow	<u>12</u>
Total		<u>32</u>

Number of equations and specifications:

Specified values		
Hot gas:	T , p , and 4 component flows	6
Cool gas:	T and p	2
Water in:	T and p	2
Water out:	T and p	2
Specified in the energy balance:		
	Q and W	2
	PE and KE (in 4 streams)	8
Material balances:	4 species balances plus water	5
Energy balance:		1
H in each stream is a function of the specified T and p		<u>4</u>
		<u>32</u>

<i>Degrees of freedom</i>	0
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Frequently Asked Questions

1. Do you always have to solve the material balances before you solve the energy balances? No, but most problems are solved more efficiently by so doing. If you just plan to solve a complete set of equations simultaneously with an equation solver, there is no need to solve the material balances first.
2. Can you keep count of the number of degrees of freedom serially as you go along solving parts of a problem without engaging in a complete degree-of-freedom analysis at the start? Yes, particularly for complex problems in which you can uncouple sets of equations to be solved simultaneously.

SELF-ASSESSMENT TEST

Questions

1. Will including the energy balance in a set of equations used to solve a problem always add one independent equation to the set?
2. If in an open, steady-state process you have several components in each stream, will an energy balance on each component separately provide independent equations to use in the solution of a problem?
3. If in an open, unsteady-state process two streams flow out of a system, can the energy balance provide an extra independent equation to the set of material balances?

Problems

1. Examine the process displayed in Figure SAT24.2P1.

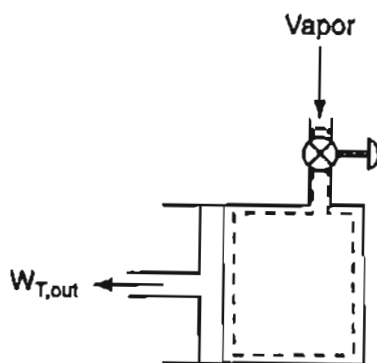


Figure SAT24.2P1

The cylinder is insulated. Initially the volume of steam contained in the cylinder by the piston is 0.1 m^3 at 200 kPa and 600 K. When the valve is opened the steam expands slowly, causing the piston to move to the left, doing work until the volume in the cylinder

is 0.2 m^3 at 200 kPa. How many degrees of freedom exist for this process? Go through the steps listed in Section 24.2 for the system identified by the dashed line in Figure SAT24.2P1.

2. You want to heat 100 lb/min of water at 100°F to 180°F . How many independent equations can you write for the process, and how many degrees of freedom exist? Refer to Figure SAT24.2P2.

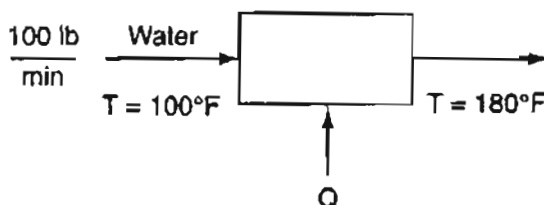


Figure SAT24.2P2

24.3 Applications of the Energy Balance to Closed Systems

Information is pretty thin stuff, unless it is mixed with experience.

Clarence Day

The first step listed in the proposed approach for solving energy balance problems (refer back to Section 24.2) is to specify the system and decide if it is open or closed. In this section we present several examples of applying the general energy balance to closed systems. To get the most out of this section you should read the problem statement, cover up the solution, and outline in your mind or on paper how you would carry out the solution of the problem. Then compare your ideas with those you have covered up. (You can peek if you get stuck.)

EXAMPLE 24.3 Application of the Energy Balance

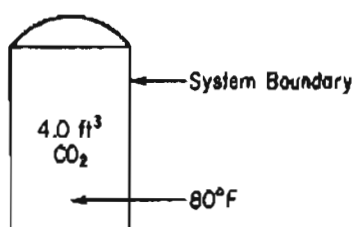
Ten pounds of CO_2 at room temperature (80°F) are stored in a fire extinguisher having a volume of 4.0 ft^3 . How much heat must be removed from the extinguisher so that 40% of the CO_2 becomes liquid?

Solution

This problem involves a closed, unsteady-state system (Figure E24.3) without reaction. You can use the CO_2 chart in Appendix J to get the necessary property values.

Steps 1, 2, 3, and 4

The specific volume of the CO_2 is $4.0/10 = 0.40 \text{ ft}^3/\text{lb}$, hence you can find on the CO_2 chart at $\hat{V} = 0.40$ and $T = 80^\circ\text{F}$ that CO_2 is a gas at the start of the process. The reference state for the CO_2 chart is -40°F , saturated liquid. The pressure is 300 psia and $\Delta\hat{H} = 160 \text{ Btu/lb}$.

**Figure E24.3****Step 5**

Basis: 10 lb CO_2

Steps 6 and 7

The material balance is trivial—the mass in the system is constant at 10 lb. In the energy balance

$$\Delta E = Q + W$$

W is zero because the volume of the system is fixed, hence with $\Delta KE = \Delta PE = 0$ inside the system

$$Q = \Delta U = \Delta H - \Delta(pV)$$

You cannot obtain values of $\Delta\hat{U}$ from the CO_2 chart, only values of $\Delta\hat{H}$, by following the constant-volume line of $0.40 \text{ ft}^3/\text{lb}$ to the spot where the quality is 0.6. Hence the final state is fixed, and all the final properties can be identified, namely

$$\Delta\hat{H}_{\text{final}} = 81 \text{ Btu/lb}$$

$$p_{\text{final}} = 140 \text{ psia}$$

You can conclude that the degrees of freedom for the problem are zero, with one equation in one unknown to be solved for Q .

Steps 7, 8, and 9

$$Q = \left\{ (81 - 160) - \left[\frac{(140)(144)(0.40)}{778.2} - \frac{(300)(144)(0.40)}{778.2} \right] \right\} 10$$

$$= -672 \text{ Btu (heat is removed)}$$

EXAMPLE 24.4 Application of the Energy Balance to Plasma Etching

Argon gas in an insulated plasma deposition chamber with a volume of 2 L is to be heated by an electric resistance heater. Initially the gas, which can be treated as an ideal gas, is at 1.5 Pa and 300 K. The 1000-ohm heater draws current at 40 V for 5 minutes (i.e., 480 J of work is done on the system by its surroundings). What is the final gas temperature and pressure in the chamber? The mass of the heater is 12 g and its heat capacity is 0.35 J/(g)(K). Assume that the heat transfer through the walls of the chamber from the gas at this low pressure and in the short time period considered is negligible.

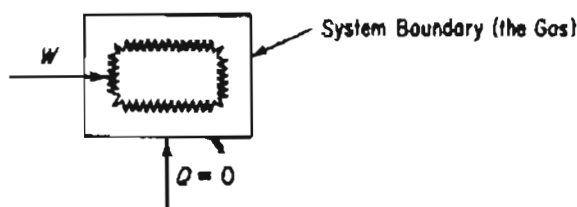


Figure E24.4

Solution

No reaction occurs. The fact that the heater coil is “heated” inside the system does not mean that heat transfer takes place to the selected system from the surroundings. The system does not exchange mass with the surroundings, and is unsteady state.

Steps 1, 2, 3, and 4

Pick the system as the gas plus the heater, as shown in Figure E24.4. Because of the assumption about the heat transfer, $Q = 0$. W is given as +480 J (work done on the system) in 5 minutes.

Step 5

Basis: 5 minutes

Steps 6 and 7

The general energy balance (with $\Delta PE = \Delta KE = 0$ inside the system) is

$$\Delta E = \Delta U = Q + W$$

and reduces to $\Delta U = 480$ J

The assumption that the gas is ideal simplifies the solution because for an ideal gas

$$pV = nRT$$

Initially we know p , V , and T , and thus can calculate the amount of the gas:

$$n = \frac{pV}{RT} = \frac{1.5 \text{ Pa} \left| \frac{2 \text{ L}}{1 \text{ L}} \right| \frac{10^{-3} \text{ m}^3}{1 \text{ L}} \left| \frac{1 (\text{g mol})(\text{K})}{8.314 (\text{Pa})(\text{m}^3)} \right|}{300 \text{ K}}$$

$$= 1.203 \times 10^{-6} \text{ g mol}$$

You are given the heater mass and a heat capacity of $C_v = 0.35 \text{ J}/(\text{g})(\text{K})$, and the C_v of the gas can be calculated. Since $C_p = \frac{5}{2}R$ (see Table 23.1), then

$$C_v = C_p - R = \frac{5}{2}R - R = \frac{3}{2}R$$

You have to pick a reference temperature for the calculations. The most convenient reference state is 300K. Then ΔU for the gas and the heater can be calculated, assuming both the heater and the gas end up at the same temperature:

Gas:

$$\Delta U_g = 1.203 \times 10^{-6} \int_{300}^T C_v dT' = 1.203 \times 10^{-6} \left(\frac{3}{2}R \right) (T - 300)$$

Heater:

$$\Delta U_h = 12 \text{ g} \left(\frac{0.35 \text{ J}}{(\text{g})(\text{K})} \right) (T - 300)$$

The mass balance is trivial—the mass in the chamber does not change. The unknown is T , and one equation is involved, the energy balance, so that the degrees of freedom are zero.

Steps 8 and 9

Because $\Delta U = 480 \text{ J}$, you can calculate T from the energy balance

$$\Delta U = 480 \text{ J} = \overbrace{(12)(0.35)(T - 300)}^{\text{heater}} + \overbrace{(2.302 \times 10^{-6})\left(\frac{3}{2}\right)(8.314)(T - 300)}^{\text{gas}}$$

$$T = 414 \text{ K}$$

The final pressure is

$$\frac{p_2 V_2}{p_1 V_1} = \frac{n_2 R T_2}{n_1 R T_1}$$

or

$$p_2 = p_1 \left(\frac{T_2}{T_1} \right) = 1.5 \left(\frac{414}{300} \right) = 2.07 \text{ Pa}$$

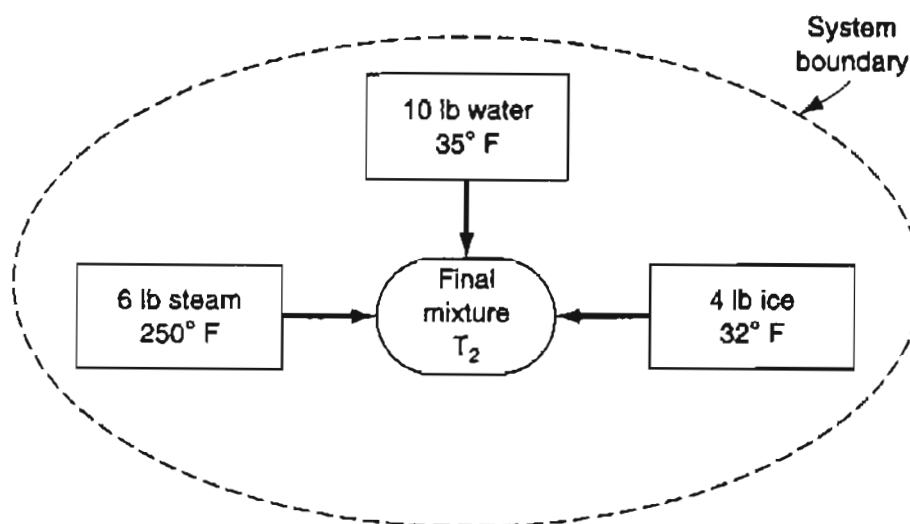
EXAMPLE 24.5 Energy Balance Applied to a Batch Process

Suppose you mix 10 pounds of water at 35°F, 4.00 lb of ice at 32°F, and 6.00 lb of steam at 250°F and 20 psia together in a container of fixed volume. What is the final temperature of the mixture? How much steam condenses? Assume that the volume of the vessel is constant with a value equal to the initial volume of the steam, and that the vessel is insulated.

Solution**Steps 1, 2, 3, and 4**

In picking a system, if you select the system depicted in Figure E24.5, you define a batch process that takes place in a closed system with $Q = 0$ and $W = 0$. Of course, you could select three separate systems for the ice, water, and steam, respectively, plus one for the final material, but the answer to the problem will be the same. Let T_2 be the final temperature in the system. The system consists of a total of 20 lb of H_2O in three phases initially, and in one or two phases at the final state. ΔKE and ΔPE are equal to 0. The energy balance reduces to $\Delta U = 0$.

To solve the problem you have to get the properties of water at the initial and final conditions in the system. If you use many versions of the AE steam tables, you can only retrieve \hat{H} values, not the \hat{U} values that you want (and could get from SI steam tables or the AE steam tables in this book). Thus, you would also have to collect values of p and \hat{V} at the initial and final states along with values of \hat{H} . To avoid having to calculate $\Delta \hat{U}$ from $\Delta \hat{H} - \Delta(p\hat{V})$, we will get the values of \hat{U} from the CD in the back of this book.

**Figure E24.5**

The properties you need are:

	$T(^{\circ}\text{F})$	$\hat{U}(\text{Btu/lb})$	$\hat{V}(\text{ft}^3/\text{lb})$
Ice	32	-143.6*	ignore
Water	35	3.025	0.0162
Steam @ 20 psia	250	1092.25	20.80

*value of $-\Delta\hat{H}_{\text{fusion}}$

What is the reference state implied by the above data?

The volume of the container is fixed at the initial volume of the steam, namely $(6)(20.80) = 124.80 \text{ ft}^3$; you can ignore the volumes of the ice and water in the calculations, as they are so small.

Step 5

The basis is 20 lb of water at the given conditions.

$$\text{Basis: } \begin{cases} 4 \text{ lb of ice at } 32^{\circ}\text{F} \\ 10 \text{ lb of H}_2\text{O at } 35^{\circ}\text{F} \\ 6 \text{ lb of steam at } 250^{\circ}\text{F and } 20 \text{ psia} \end{cases}$$

Steps 6 and 7

The unknowns are T_2 , the final temperature of the system, the quality x at the final state, \hat{U}_2 , and \hat{V}_2 . However, all of these variable are related in the steam tables so that once T_2 is chosen, the values of all of the other variables are known if the final state is assumed to be saturated. If it is not saturated, then values of two properties must be known to get the remaining ones, so that some information would have to be given about the final pressure in the system.

What is the final specific volume in the system? It is

$$\frac{124.80 \text{ ft}^3}{20 \text{ lb}} = 6.42 \text{ ft}^3/\text{lb}$$

What is the final specific internal energy of the system? It is the initial internal energy divided by the initial mass because no heat transfer or work occurs

$$\frac{[4(-143.6) + 10(3.025) + 6(1092.25)] \text{ Btu}}{20 \text{ lb}} = 357.9 \text{ Btu/lb}$$

To calculate the quality of the vapor in the final state of the system, you can make use of the above two values

$$(1 - x)\hat{V}_{\text{liq}} + x\hat{V}_{\text{vap}} = 6.42 \quad (\text{a})$$

$$(1 - x)\hat{U}_{\text{liq}} + x\hat{U}_{\text{vap}} = 357.9 \quad (\text{b})$$

Let's ignore the volume of the liquid—it is so small. Then

$$x = \frac{6.42}{\hat{V}_{\text{vap}}} \quad (\text{c})$$

Use of the steam tables requires a trial-and-error solution. You assume a T_2 , look up \hat{U} and \hat{V} for the liquid and vapor, use Equation (c) to get x , and determine if Equation (b) is satisfied. By assuming different temperatures, you can bracket 357.9, and interpolate to get T_2 .

Assume $T_2 = 200^\circ\text{F}$

	Liquid	Vapor	
\hat{U} (Btu/lb)	168.11	1073.96	
\hat{V} (ft ³ /lb)	0.017	33.601	$x = 6.42/33.601 = 0.191$
$0.809(168.11) + 0.191(1073.96) = 337.11$ too low			

Assume $T_2 = 210^\circ\text{F}$

\hat{U} (Btu/lb)	178.17	1076.83	
\hat{V} (ft ³ /lb)	0.017	27.788	$x = 6.42/27.788 = 0.231$
$0.769(178.17) + 0.231(1076.83) = 385.76$ too high			

Linear interpolation between the two temperatures gives the final temperature as 205°F and a quality of 0.21. The final state is $20(0.21) = 4.2$ lb vapor, so that $6 - 4.2 = 1.8$ lb of steam condenses.

SELF-ASSESSMENT TEST

Questions

- Suppose that a selected system is the fluid in a Dewar bottle (in order to make $Q = 0$). Since the fluid cannot move the bottle walls, $W = 0$. Furthermore, suppose that a ball affixed to the inside top of the Dewar is released somehow (with a negligible expenditure of energy), and drops to the bottom of the Dewar. What specific terms in the energy balance for the system change?

Problems

- Liquid oxygen is stored in a 14,000 L storage tank. When charged, the tank contains 13,000 L of liquid in equilibrium with its vapor at 1 atm pressure. What is the (a) temperature, (b) mass, and (c) quality of the oxygen in the vessel? The pressure relief valve of

the storage tank is set at 2.5 atm. If heat leaks into the oxygen tank at the rate of 5.0×10^6 J/hr, (d) when will the pressure relief valve open, and (e) what will be the temperature in the storage tank at that time?

Data: at 1 atm, saturated, $\hat{V}_l = 0.0281$ L/g mol, $\hat{V}_g = 7.15$ L/g mol, $\Delta\hat{H} = -133.5$ J/g; at 2.5 atm, saturated, $\Delta\hat{H} = -116.6$ J/g.

2. Suppose that you fill an insulated Thermos to 95% of the volume with ice and water at equilibrium and securely seal the opening.
 - a. Will the pressure in the Thermos go up, down, or remain the same after 2 hours?
 - b. After 2 weeks?
 - c. For the case in which after filling and sealing, the Thermos is shaken vigorously, what will happen to the pressure?
3. An 0.25-liter container initially filled with 0.225 kg of water at a pressure of 20 atm is cooled until the pressure inside the container is 100 kPa.
 - a. What are the initial and final temperatures of the water?
 - b. How much heat was transferred from the water to reach the final state?
4. In a shock tube experiment, the gas (air) is held at room temperature at 15 atm in a volume of 0.350 ft^3 by a metal seal. When the seal is broken, the air rushes down the evacuated tube, which has a volume of 20 ft^3 . The tube is insulated. In the experiment:
 - a. What is the work done by the air?
 - b. What is the heat transferred to the air?
 - c. What is the internal energy change of the air?
 - d. What is the final temperature of the air after 3 min?
 - e. What is the final pressure of the air?

24.4 Application of the Energy Balance to Open Systems

As a chemical engineer you will encounter a wide variety of processes in any plant. Most of the processes will be modeled as open (flow), steady-state systems. Operations such as the transport of solids and liquids, heat exchange, evaporation, and so on involve open systems. You will find that even in complex plants the essentials of analysis reduce to the review of the material and energy flows, as illustrated in Figure 24.3. At each stage there can be loss of material and energy, losses that can go into the environment, losses that engineers try to reduce economically.

In what follows we present some relatively simple examples of applying energy balances. Look at Chapter 31 (on the CD in the back of this book) to view more complicated examples that resemble units of plants in industry.

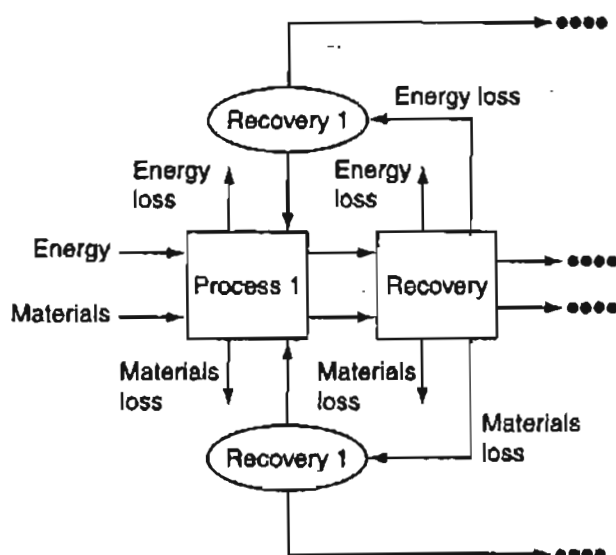


Figure 24.3 General energy and materials flow in a complex plant.

EXAMPLE 24.6 Application of the Energy Balance to Pumping Water

Water is being pumped from the bottom of a well 15 ft deep at the rate of 200 gal/hr into a vented storage tank to maintain a level of water in a tank 165 ft above the ground. To prevent freezing in the winter a small heater puts 30,000 Btu/hr into the water during its transfer from the well to the storage tank. Heat is lost from the whole system at the constant rate of 25,000 Btu/hr. What is the temperature of the water as it enters the storage tank, assuming that the well water is at 35°F? A 2-hp pump is being used to pump the water. About 55% of the rated horsepower goes into the work of pumping and the rest is dissipated as heat to the atmosphere.

Solution

Steps 1, 2, 3, and 4

Let the system (assume an open, steady-state system) consist of the well inlet, the piping, the pump, and the outlet at the storage tank. See Figure E24.6.

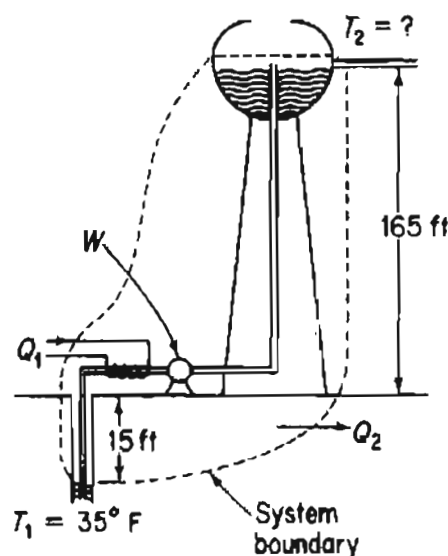


Figure E24.6

Step 5

Basis: 1 hr of operation.

Steps 6 and 7

The material balance is 200 gal of water entering and 200 gal leaving in an hour. The energy balance is

$$\Delta E = Q + W - \Delta[(\hat{H} + \widehat{KE} + \widehat{PE})m]$$

You can simplify the energy balance as follows:

1. The process is in the steady state, so that $\Delta E = 0$.
2. $m_1 = m_2 = m$.
3. $\Delta KE \cong 0$ because we will assume that $v_1 = v_2 \cong 0$.

Then

$$0 = Q + W - \Delta[(\hat{H} + \widehat{PE})m]$$

Only the value of ΔH at the top of the tank is unknown, but it can be calculated from the energy balance. *If you pick a reference temperature for \hat{H} at 35°F (the input temperature), then the enthalpy of the input stream will be zero.* Do you see why? The temperature difference is $(T_{in} - 35) = (35 - 35) = 0$. Then ΔH can be calculated as $H_2 - 0$. The outlet temperature can be determined from the calculation for the property \hat{H} if C_p is assumed to be constant

$$\Delta H = m\Delta\hat{H} = m \int_{T=35^\circ\text{F}}^{T_2} C_p dT = mC_p(T_2 - 35)$$

Would the equation differ if you picked another reference temperature? No, because the reference values for \hat{H} cancel out—only the values of \hat{H} at the initial and final states are used to get $\Delta\hat{H}$.

The problem has a unique solution because the degrees of freedom are zero. Check this conclusion.

Steps 8 and 9

The total mass of water pumped is

$$\frac{200 \text{ gal}}{\text{hr}} \left| \frac{8.33 \text{ lb}}{1 \text{ gal}} \right| = 1666 \text{ lb}$$

The potential energy change is

$$\begin{aligned} \Delta PE = m\Delta\widehat{PE} = mg\Delta h &= \frac{1666 \text{ lb}_m}{\text{hr}} \left| \frac{32.2 \text{ ft}}{\text{s}^2} \right| \left| \frac{180 \text{ ft}}{\text{ft}} \right| \left| \frac{(\text{s}^2)(\text{lb}_f)}{32.2(\text{ft})(\text{lb}_m)} \right| \left| \frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)} \right| \\ &= 385.4 \text{ Btu} \end{aligned}$$

The heat lost by the system is 25,000 Btu while the heater puts 30,000 Btu into the system; hence the net heat exchange is

$$Q = 30,000 - 25,000 = 5000 \text{ Btu}$$

The rate of work being done on the water by the pump is

$$\dot{W} = \frac{2 \text{ hp}}{0.55} \left| \frac{33,000(\text{ft})(\text{lb}_f)}{(\text{min})(\text{hp})} \right| \frac{60 \text{ min}}{\text{hr}} \frac{\text{Btu}}{778(\text{ft})(\text{lb}_f)} = 2800 \text{ Btu/hr}$$

hence $W = 2800 \text{ Btu}$

$$\Delta H \text{ can be calculated from: } Q + W = \Delta H + \Delta PE$$

$$5000 + 2800 = \Delta H + 385$$

$$\Delta H = 7415 \text{ Btu}$$

Because the temperature range considered is small, the heat capacity of liquid water may be assumed to be constant and equal to $1.0 \text{ Btu}/(\text{lb})(^\circ\text{F})$ for the problem. Thus,

$$7415 = \Delta H = mC_p \Delta T = 1666(1.0)(T_2 - 35)$$

$$\Delta T \cong 4.5^\circ\text{F} \text{ temperature rise, hence, } T_2 = 39.5^\circ\text{F}.$$

EXAMPLE 24.7 Application of the Energy Balance to Heating a Biomass

Steam at 250°C saturated (that is used to heat a fermentation broth) enters the steam chest of a fermentor. The steam chest is segregated from the biomass in the fermentor. Assume that the steam is completely condensed in the steam chest. The rate of the heat loss from the fermentor to the surroundings is 1.5 kJ/s . The material to be heated is placed in the fermentor at 20°C and at the end of the heating it is at 100°C . If the charge consists of 150 kg of material with an average heat capacity of $C_p = 3.26 \text{ J}/(\text{g})(\text{K})$, how many kilograms of steam are needed per kilogram of charge? The charge remains in the vessel for 1 hr .

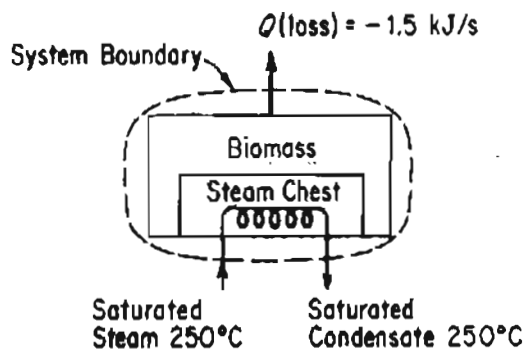


Figure E24.7a

Solution**Steps 1, 2, 3, and 4**

Figure E24.7a defines the system and shows the known conditions. If the system is the biomass plus the steam chest, the process is open but not a steady state one because the temperature of the biomass increases. Zero degrees of freedom exist so that the problem has a solution.

Step 5

Basis: 1 hr of operation (150 kg of charge)

Steps 6, 7, and 8

The steam is the only material entering and leaving the system, and $m_1 = m_2$ of the steam, hence the material balance is simple. The energy balance is

$$\Delta E = Q + W - \Delta[(\hat{H} + \hat{KE} + \hat{PE})m] \quad (a)$$

Let us simplify the energy balance

1. The process is not in the steady state, so $\Delta E \neq 0$.
2. We can safely assume that $\Delta KE = 0$ and $\Delta PE = 0$ inside the system.
3. $W = 0$.
4. ΔKE and ΔPE of the entering and exiting material are zero.

Consequently, Equation (a) becomes

$$\Delta E = \Delta U = Q - \Delta[(\hat{H})m] \quad (b)$$

where ΔU can be calculated from just the change in state of the biomass, and does not include the water in the steam chest because we will assume that there was no water in the steam chest at the start of the hour and none in the steam chest at the end of the hour. (You could alternately assume the mass of water in the steam chest and its state were the same at $t = 0$ and $t = 1$ hour.) Let $m_1 = m_2 = m_{\text{steam}}$ be the mass of steam that goes through the steam chest in 1 hour. Let the heat capacity of the biomass, $C_{p, \text{biomass}}$, be constant with respect to temperature. Then you can calculate the values of the terms in Equation (b):

- (a) $\Delta U = \Delta H - \Delta(pV) = \Delta H = m_{\text{biomass}} C_{p, \text{biomass}} (373 - 293)\text{K}$ [because we know that $\Delta(pV)$ for the liquid or solid charge is negligible]. Thus

$$\Delta U = \Delta H_{\text{biomass}} = \frac{150 \text{ kg}}{1} \left| \frac{3.26 \text{ kJ}}{(\text{kg})(\text{K})} \right| \frac{(373 - 293)\text{K}}{1} = 39,120 \text{ kJ}$$

- (b) The heat loss is given as $Q = -1.50 \text{ kJ/s}$

$$\frac{-1.50 \text{ kJ}}{\text{s}} \left| \frac{3600 \text{ s}}{1 \text{ hr}} \right| \frac{1 \text{ hr}}{1} = -5400 \text{ kJ}$$

- (c) The specific enthalpy change for the steam (if the changes consist only of the $\Delta \hat{H}$ of condensation) can be determined from the steam tables. The $\Delta \hat{H}_{vap}$ of saturated steam at 250°C is 1701 kJ/kg, so that

$$\Delta \hat{H}_{steam} = -1701 \text{ kJ/kg}$$

Introduction of all these values into Equation (b) gives

$$39,120 \text{ kJ} = -\left(-1701 \frac{\text{kJ}}{\text{kg steam}}\right)(m_{steam} \text{ kg}) - 5400 \text{ kJ} \quad (c)$$

from which the kilograms of steam per hour, m_{steam} , can be calculated as

$$m_{steam} = \frac{44,520 \text{ kJ}}{1701 \text{ kJ}} \left| \frac{1 \text{ kg steam}}{1 \text{ kg}} \right| = 26.17 \text{ kg steam}$$

Thus

$$\frac{26.17 \text{ kg steam}}{150 \text{ kg charge}} = 0.174 \frac{\text{kg steam}}{\text{kg charge}}$$

Next, let us look at the problem from a different viewpoint. If one system had been chosen to be the biomass inside the fermentor and the other system chosen to be the steam chest and lines, we would have a configuration, as shown in Figure E24.7b. Under these circumstances heat would be transferred from the steam chest to the biomass. From an energy balance on the steam chest (with no accumulation)

$$Q_{system II} = \Delta H_{steam} \quad (d)$$

As indicated in Fig. E24.7b, the value of $Q_{system II}$ is negative.

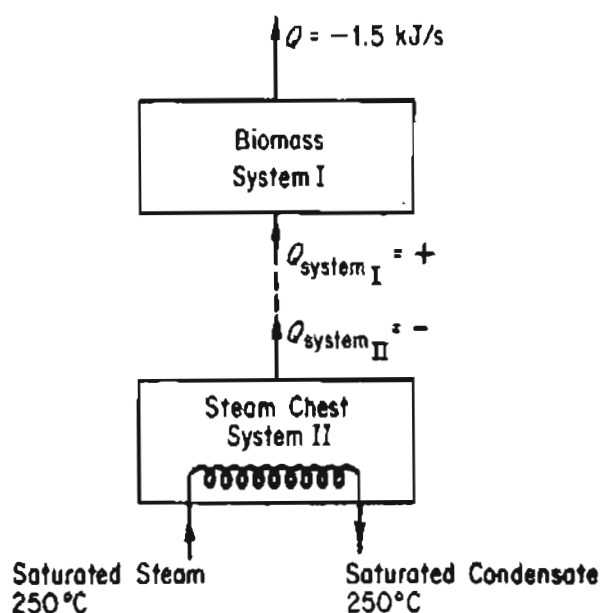


Figure E24.7b

The energy balance for system I with no mass flow in or out of system I is

$$\Delta E_{\text{system I}} = \Delta U_{\text{biomass}} \cong \Delta H_{\text{biomass}} = Q_I - 5400 \quad (\text{e})$$

Q_{II} and Q_I have opposite values because heat is removed from system II and added to system I. Because

$$Q_{II} = \Delta H_{\text{steam}} = (-1701)m_{\text{steam}}$$

you know that $Q_I = +(1701)m_{\text{steam}}$, and Equation (e) becomes the same as Equation (c).

EXAMPLE 24.8 Sterilization of a Fermentation Medium

For a biological media (or medical instruments) the primary objective of sterilization (pasteurization) is to destroy undesirable microorganisms. At the same time, you want to avoid nutrient degradation and minimize costs. Figure E24.8 shows a process in which a biological media passes through a sterilizer heated by hot water. The return hot water is heated by condensing steam. The total heat loss from the process is 1.63 kW. Figure E24.8 shows the conditions for the process flows. Calculate the flow rate of the steam entering the steam heater.

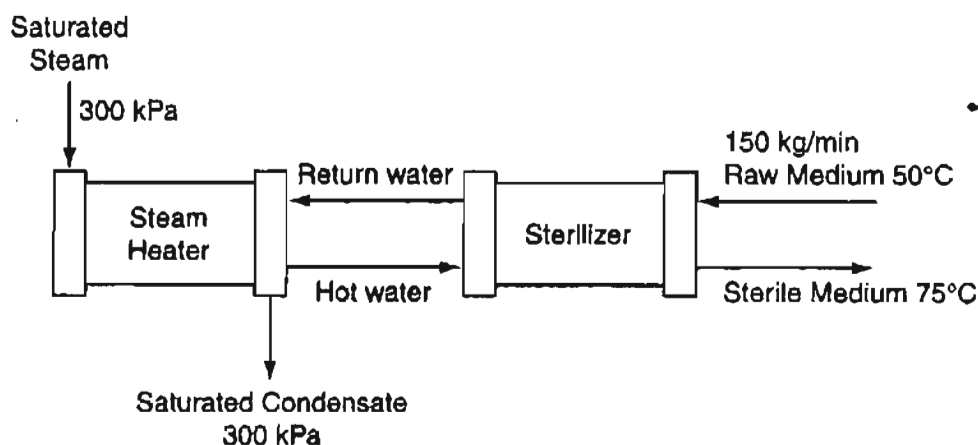


Figure E24.8

Solution

Both material and energy balances are involved in the solution of this problem.

Steps 1–4

The basic data are in Figure E24.8. From the steam tables (assuming that the biomedium has the properties of water), you can obtain the necessary enthalpies:

	$\Delta \hat{H}$ (kJ/kg)
Water, 50°C	207.5
Water, 75°C	310.3
Steam, saturated, 300 kPa	2724.9
Water, saturated, 300 kPa	561.2

Step 5

Basis: 150 kg biomedica (1 min)

Steps 6 and 7

For the calculations you can pick as the designated system (a) the sterilizer, (b) the steam heater, or (c) the whole process. Let's pick (c) because the properties of the hot water in the streams between the two pieces of equipment are unknown. You can assume that the system is open and steady state.

The material balances are quite simple: what goes in the sterilizer comes out, namely 150 kg of biomedica, and what goes in the steam heater comes out, but we do not know the value. Let's call it m kg.

The degrees of freedom are zero because you have only one unknown quantity, m , and you can write down one energy balance as follows. Because the system is in the steady state with no work, KE , or PE involved, the general energy balance reduces to

$$Q = \Delta H = H_{\text{out}} - H_{\text{in}}$$

$$\frac{1.63 \text{ kW}}{(1 \text{ W})(\text{s})} \frac{1 \text{ J}}{1 \text{ min}} \frac{60 \text{ s}}{1 \text{ min}} = \frac{150 \text{ kg } F}{\text{kg } F} \frac{310.3 \text{ kJ}}{\text{kg } F} + \frac{m \text{ kg water}}{\text{kg water}} \frac{561.2 \text{ kJ}}{\text{kg water}}$$

$$- \frac{150 \text{ kg } F}{\text{kg } F} \frac{207.5 \text{ kJ}}{\text{kg } F} - \frac{m \text{ kg steam}}{\text{kg steam}} \frac{2724.9 \text{ kJ}}{\text{kg steam}}$$

$$m = 7.08 \text{ kg of steam per minute} \quad 7.18$$

EXAMPLE 24.9 Use of Combined Material and Energy Balances to Solve a Distillation Problem

A feed of a mixture of benzene (Bz) and toluence (Tol) is separated as shown in Figure E24.9a. Calculate the values of the distillate (D), the bottoms (B), the heat duty (heat removed by the water) in the condenser (Q_C), and the heat duty (input) to the reboiler (Q_R). The recycle ratio R/D is 4.0.

Solution

The entering and exit streams F , D , and B are all liquids (presumably saturated liquids). The system is open and steady state ($\Delta E = 0$).

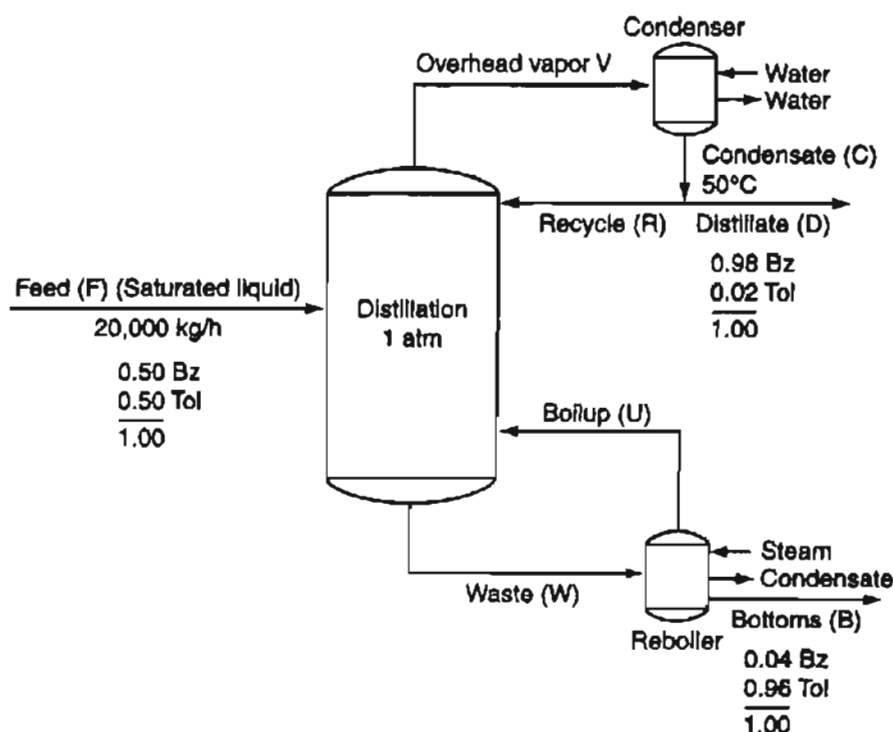


Figure E24.9a

Steps 1, 2, 3, and 4

Figure E24.9a contains most of the information pertaining to the problem. Enthalpy data will be taken from Figure E24.9b at the cost of some accuracy to save you time.

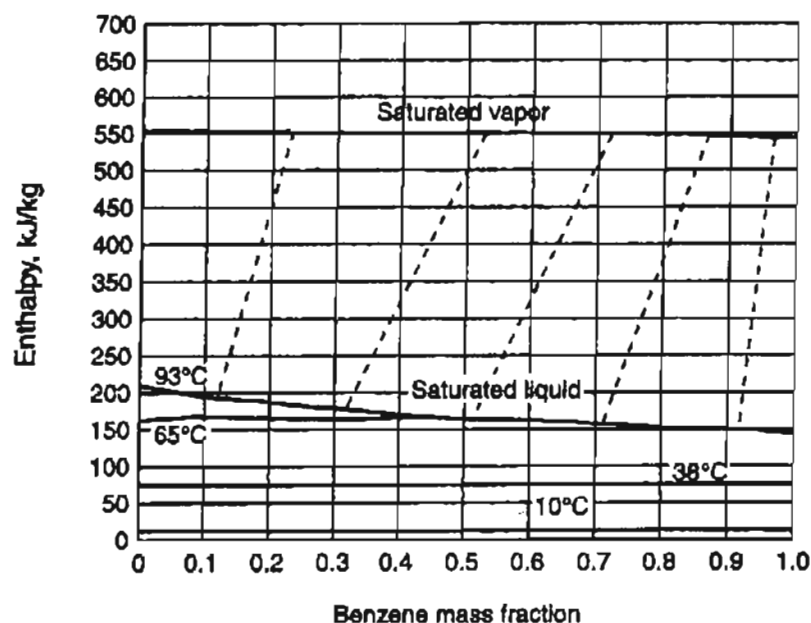


Figure E24.9b The ends of the dashed lines show the equilibrium compositions between the liquid and vapor.

Step 5

Basis: 1 hour \equiv 20,000 kg of feed

Steps 6 and 7

Examination of the problem shows that the material balances can be uncoupled from the energy balance if you *pick the overall process* as the system. For the material balances the degree-of-freedom analysis is

Variables:	B and D	2
Material balances:	Bz and Tol	<u>2</u>
Degrees of freedom		0

Steps 8 and 9

You can write three material balances, only two of which are independent

$$\text{Total} \quad 20,000 \quad = D + B$$

$$Bz: \quad (0.50)(20,000) = 0.98D + 0.04B$$

$$Tol: \quad (0.50)(20,000) = 0.02D + 0.96B$$

Solve using the last two of the three equations to get

$$D = 9.8 \times 10^3 \text{ kg} \quad B = 1.02 \times 10^4 \text{ kg}$$

Then $R = 4(D) = 3.92 \times 10^4 \text{ kg}$.

Step 10

Check via the total equation

$$0.98 \times 10^4 + 1.02 \times 10^4 = 2.00 \times 10^4$$

Next let's start examining the general energy balance. You can reduce the number of variables involved by specifying that $W = 0$ for the system and $PE = KE = 0$ for each stream. The energy balance reduces to $Q = \Delta H$. The degrees-of-freedom analysis for the steady state system will be based on starting by considering every variable.

Number of variables (substitute T and p for H):

For F :	m_{Bz}^F, m_{Tol}^F, T^F , and p^F	4
For D :	m_{Bz}^D, m_{Tol}^D, T^D , and p^D	4
For B :	m_{Bz}^B, m_{Tol}^B, T^B , and p^B	4
For the condenser:	Q_C	1
For the boiler:	Q_R	1
		<u>14</u>

Number of equations:

Specifications of values of variables:

For F : m_{Bz}^F , m_{Tot}^F , T^F , and p^F 4

(F is saturated liquid at its boiling point)

For D : m_{Bz}^D , m_{Tot}^D , T^D , and p^D 4

(pressure assumed to be the vapor pressure at T^D)

For B : m_{Bz}^B , m_{Tot}^B , T^B , and p^B 4

(pressure assumed to be the vapor pressure at T^B)

Energy balance on the total system $\frac{1}{13}$

Clearly one more equation is needed to make the degrees of freedom zero. We have used all of the independent material balances for the system comprised of the total process, but you can make an independent energy balance around the condenser as a system. First you have to calculate V . Note that V at the top of the column does not have the same value as the vapor that rises up from the bottom of the column.

$$V = R + D = 4D + D = 5D = 4.90 \times 10^4 \text{ kg}$$

Assume V is in equilibrium with D at 50°C .

From Figure E24.8b the enthalpy data are

Variable	State	kg	Approximate $\Delta H(\text{kJ/kg})$
F	Saturated liquid, $\omega_{Bz} = 0.50$	20,000	165
B	Saturated liquid, $\omega_{Bz} = 0.04$	10,200	205
D	Saturated liquid, 50°C $\omega_{Bz} = 0.98$	9,800	100
R	Saturated liquid, 50°C $\omega_{Bz} = 0.98$	39,200	100
V	Saturated vapor, $\omega_{Bz} = 0.98$	49,000	540

over specified

An energy balance about the condenser will yield Q_C .

$$(39,200 + 9800)(100) - (49,000)(540) = Q_C = -2.38 \times 10^7 \text{ kJ (heat removed)}$$

An energy balance about the whole system is easier to use than a balance about the reboiler because the values of U and W are not involved.

Finally,

$$(9800)(100) + (10,200)(205) - (20,000)(165) = Q_R + Q_C = Q_R - 2.38 \times 10^7$$

$$Q_R = 2.36 \times 10^7 \text{ kJ}$$

SELF-ASSESSMENT TEST

Questions

1. What are the differences between the degree-of-freedom analysis for a problem involving material and energy balances and that of a problem involving material balances only.
2. In problems involving energy balances, is it better to pick the overall process as the system, or pick subsections of the overall process?
3. Explain how the reference state for energy balance calculations can make the enthalpy of a stream have a value of zero.
4. If a pipe entering a process has material in it, but no material is flowing, is the enthalpy of the material in the pipe zero insofar as the energy balance is concerned?

Problems

1. In a refinery a condenser is set up to cool 1000 lb/hr of benzene that enters at 1 atm, 200°F, and leaves at 171°F. Assume negligible heat loss to the surroundings. How many pounds of cooling water are required per hour if the cooling water enters at 80°F and leaves at 100°F?
2. In a steady-state process, 10 g mol/s of O₂ at 100°C and 10 g mol/s of nitrogen at 150°C are mixed in a vessel that has a heat loss to the surroundings equal to 209(*T* – 25) J/s, where *T* is the temperature of the gas mixture in °C. Calculate the gas temperature of the exit stream in °C. Use the following heat capacity equations:

$$\text{O}_2: C_p = 6.15 + 3.1 \times 10^{-3} T$$

$$\text{N}_2: C_p = 6.5 + 1.25 \times 10^{-3} T$$

where *T* is in *K* and *C_p* is in cal/(g mol)(K).

3. An exhaust fan in a constant-area well-insulated duct delivers air at an exit velocity of 1.5 m/s at a pressure differential of 6 cm H₂O. Thermometers show the inlet and exit temperatures of the air to be 21.1°C and 22.8°C, respectively. The duct area is 0.60 m². Determine the power requirement for the fan.
4. A water system is fed from a very large tank, large enough so that the water level in the tank is essentially constant. A pump delivers 3000 gal/min in a 12-in.-ID pipe to users 40 ft below the tank level. The rate of work delivered to the water is 1.52 hp. If the exit velocity of the water is 8.5 ft/s and the water temperature in the reservoir is the same as in the exit water, estimate the heat loss per second from the pipeline by the water in transit.

Thought Problems

1. Liquid was transferred by gravity from one tank to another tank of about the same height several hundred meters away. The second tank overflowed. What might cause such overflow?

2. A proposal to the Department of Energy was as follows: "The principal investigators planned to drive a turbine placed at the bottom of a tower high enough that the energy obtained from each pound of water, when converted to electricity by a generator run by the turbine, would be sufficient to electrolyze that pound of water. The resulting gas mixture, being lighter than air, would rise through an adjoining shaft to the top of the tower, where the gases would be burned to water vapor. The water would be condensed, and returned down the tower. The fact that the system would not be 100% efficient would not prevent operation, as the tower could be made higher than the theoretical height, producing enough additional power to offset losses. Overall power would come from the lifting effect of the rising gases, from the heat generated from the burning gases, and by use of the superheated steam formed by the combustion to power a turbine."

Explain whether or not this process would be successful, and your reasons for your answer.

3. When the use of heating equipment is temporarily discontinued because production is interrupted or because of the nature of the process, energy can usually be saved by allowing the equipment to cool down and then reheating. Some data have been collected as follows for an oil-fired furnace:

Temp. (°F)	Cooling time (hr)	Reheating time (hr)	Operating power at T (MBtu/hr)	Energy required to reheat to T (MBtu)
2200	0	0	10.2	0
2100	0.7	0.6	9.7	12
2000	1.7	1.3	9.2	29
1900	2.4	1.6	8.8	40
1800	3.4	2.0	8.3	49
1700	4.0	2.3	7.3	60
1600	4.9	2.6	7.2	70
1500	5.8	2.9	6.8	79
1400	6.5	3.2	6.4	80

You are told that the furnace now at 2200°F is to be shut down for 8 hours, but you must be prepared to have it back up to 2000°F subsequently. What schedule would you recommend to the operator as being the most efficient?

Discussion Problems

1. A magazine (*Environ. Sci. Technol.*, 25, 1953 [1991]) reported as follows: A novel scheme for generating electricity with compressed air produced by ocean wave action is being patented named MOTO (Motion of the Ocean). The scheme might also be engineered to produce hydrogen from water or potable water. MOTO consists of a network of 30-foot diameter toroids riding up and down on 8-foot diameter pilasters (see Figure DP24.4P1). Each toroid can store up to 4500 cubic feet of compressed gas at 500 psi. Ac-

According to the company, a system of three toroids could provide enough compressed air to generate 3 MW of electricity.

Can this be possible?

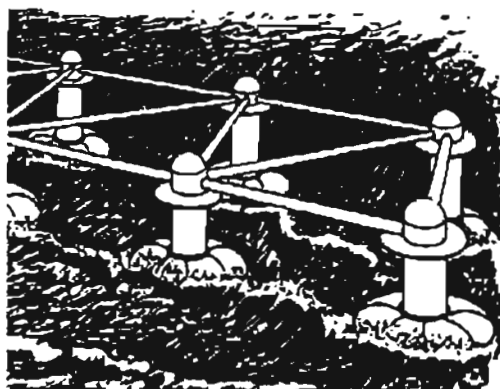


Figure DP24.4P1

2. A headline in an advertisement says, "How a chemical company generates 2,500 kW from natural gas without burning one cubic foot." Is there a plausible explanation for this claim?
3. Examine the process to generate steam shown in Figure DP24.4P3. What recommendations would you make to alter the equipment to improve the overall fuel and electricity usage?

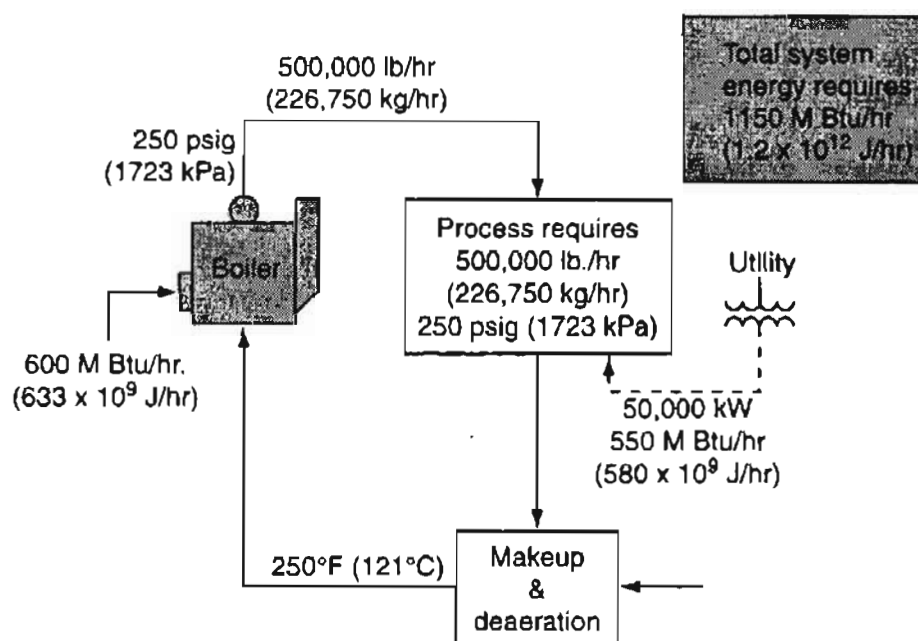


Figure DP24.4P3

Looking Back

In this chapter we illustrated how to apply the recommended problem-solving strategy to problems involving energy balances via three examples for closed systems and three examples for open systems

GLOSSARY OF NEW WORDS

Enthalpy balance The energy balance with all terms deleted leaving $\Delta H = 0$.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

ASHRAE Handbook of Fundamentals. SI version, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, GA (1993).

Balmer, R. *Thermodynamics*, West Publishing, St. Paul, MN (1990).

Van Wyler, G. J., and R. E. Sonntag. *Fundamentals of Classical Thermodynamics*, 3rd ed., John Wiley, New York (1985).

Web Sites

<http://eng.sdsu.edu/testcenter/Test/solve/systems/closed/csss/csss.html>

<http://voyager5.sdsu.edu/testcenter/features/csprocess/index.html>

PROBLEMS

***24.1** An insulated, sealed tank that is 2 ft³ in volume holds 8 lb of water at 100°F. A 1/4 hp stirrer mixes the water for 1 hour. What is the fraction vapor at the end of the hour? Assume all the energy from the stirrer enters the tank.

For this problem you do not have to get a numerical solution. Instead list the following in this order:

1. State what the system you select is.
2. Specify open or closed.
3. Draw a picture.
4. Put all the known or calculated data on the picture in the proper place.
5. Write down the energy balance (use the symbols in the text) and simplify it as much as possible. List each assumption in so doing.

6. Calculate W .
7. Lists the equations with data introduced that you would use to solve the problem.
8. Explain step by step how to solve the problem (but do not do so).

***24.2** Hot reaction products (assume they have the same properties as air) at 1000°F leave a reactor. In order to prevent further reaction, the process is designed to reduce the temperature of the products to 400°F by immediately spraying liquid water into the gas stream. Refer to Figure P24.2.

How many lb of water at 70°F are required per 100 lb of products leaving at 400°F ?

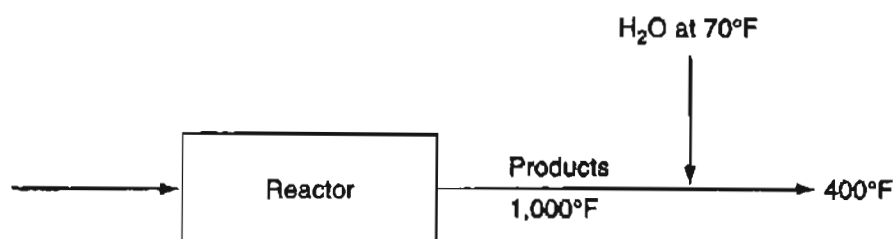


Figure P24.2

For this problem you do not have to get a numerical solution. Instead list the following in this order.

1. State what the system you select is.
 2. Specify open or closed.
 3. Draw a picture.
 4. Put all the known or calculated data on the picture in the proper places.
 5. Write down the material and energy balances (use the symbols in the text) and simplify them as much as possible; list each assumption in so doing.
 6. Insert the known data into the simplified equation(s) you would use to solve the problem.
- *24.3** How many independent equations can you write for the water flows shown in Figure P24.3?

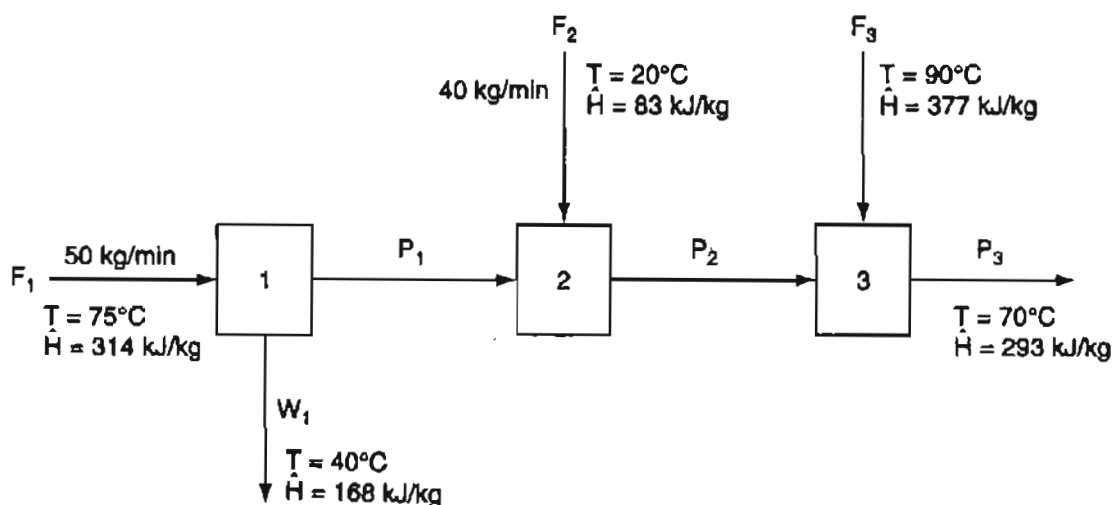


Figure P24.3

- *24.4** What would Equation (24.1) simplify to if:
- (a) there are no moving parts in the system
 - (b) $T_{\text{system}} = T_{\text{surroundings}}$
 - (c) the velocity at the inlet is that at the outlet
 - (d) the process streams enter at an elevation of 10 m and exit at an elevation of 4 m relative to earth).
- *24.5** A gas flows from a pressure of 50 atm and a temperature of 500°C to a pressure of 5 atm and a temperature of 100°C:
- (a) through a needle valve
 - (b) through an on/off valve
 - (c) through a turbine with 3 stages
 - (d) through a high velocity nozzle
- What is the difference in the enthalpy of the exit streams between each process?
- Which yields the most work?
- *24.6** Write the simplified energy balances for the following changes:
- (a) A fluid flows steadily through a poorly designed coil in which it is heated from 70°F to 250°F. The pressure at the coil inlet is 120 psia, and at the coil outlet is 70 psia. The coil is of uniform cross section, and the fluid enters with a velocity of 2 ft/sec.
 - (b) A fluid is expanded through a well-designed adiabatic nozzle from a pressure of 200 psia and a temperature of 650°F to a pressure of 40 psia and a temperature of 350°F. The fluid enters the nozzle with a velocity of 25 ft/sec.
 - (c) A turbine directly connected to an electric generator operates adiabatically. The working fluid enters the turbine at 1400 kPa absolute and 340°C. It leaves the turbine at 275 kPa absolute and at a temperature of 180°C. Entrance and exit velocities are negligible.
 - (d) The fluid leaving the nozzle of part (b) is brought to rest by passing it through the blades of an adiabatic turbine rotor and it leaves the blades at 40 psia and at 400°F.
- *24.7** Simplify the general energy balance so as to represent the process in each of the following cases. Number each term in the general balance, and state why you retained or deleted it.
- (a) A bomb calorimeter is used to measure the heating value of natural gas. A measured volume of gas is pumped into the bomb. Oxygen is then added to give a total pressure of 10 atm, and the gas mixture is exploded using a hot wire. The resulting heat transfer from the bomb to the surrounding water bath is measured. The final products in the bomb are CO₂ and water.
 - (b) Cogeneration (generation of steam both for power and heating) involves the use of gas turbines or engines as prime movers, with the exhausted steam going to the process to be used as a heat source. A typical installation is shown in Figure P24.7.
 - (c) In a mechanical refrigerator the Freon liquid is expanded through a small insulated orifice so that part of it flashes into vapor. Both the liquid and vapor exit at a lower temperature than the temperature of the liquid entering.

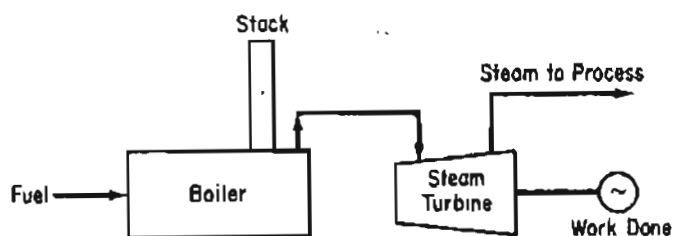


Figure P24.7

- *24.8 Ten pounds of steam is placed in a tank at 300 psia and 480°F. After cooling the tank to 30 psia, some of the steam condenses. How much cooling was required and what was the final temperature in the tank? Assume the tank itself does not absorb energy.
- *24.9 One kg of gaseous CO₂ at 550 kPa and 25°C was compressed by a piston to 3500 kPa, and in so doing 4.016×10^3 J of work was done on the gas. To keep the container isothermal, the container was cooled by blowing air over fins on the outside of the container. How much heat (in J) was removed from the system?
- ✓**24.10 A closed vessel having a volume of 100 ft³ is filled with saturated steam at 265 psia. At some later time, the pressure has fallen to 100 psia due to heat losses from the tank. Assuming that the contents of the tank at 100 psia are in an equilibrium state, how much heat was lost from the tank?
- *24.11 A large piston in a cylinder does 12,500 (ft)(lb_f) of work in compressing 3 ft³ of air to 25 psia. Five pounds of water in a jacket surrounding the cylinder increased in temperature by 2.3°F during the process. What was the change in the internal energy of the air?

$$C_{p,\text{water}} = 8.0 \frac{\text{Btu}}{(\text{lb mol})(^\circ\text{F})}$$

- *24.12 An insulated cylinder contains two gases, A and B, each held separately in place by a single-fixed plug. Initially the pressure of gas A is higher than the pressure in gas B. The plug is then released, and the system allowed to equilibrate. For the system of the two gases, what is
- the work done by the system?
 - the heat transferred to or from the system?
 - the change in internal energy of the system?
- *24.13 A small 3.1 L gas cylinder of Ne at p_1 and T_1 is attached to a large 31.7 L partially evacuated cylinder of He at p_2 and T_2 . A valve between the cylinders is opened. Determine the work done, the heat transferred, and the change in the internal energy of the gas. Assume each cylinder is well insulated.
- **24.14 Carbon dioxide cylinders, initially evacuated, are being loaded with CO₂ from a pipeline in which the CO₂ is maintained at 200 psia and 40°F. As soon as the pressure in a cylinder reaches 200 psia, the cylinder is closed and disconnected from the pipeline. If the cylinder has a volume of 3 ft³, and if the heat losses to the surroundings are small, compute:
- The final temperature of the CO₂ in a cylinder.
 - The number of pounds of CO₂ in a cylinder.

- ✓**24.15 One pound of steam at 130 psia and 600°F is expanded isothermally to 75 psia in a closed system. Thereafter it is cooled at constant volume to 60 psia. Finally, it is compressed adiabatically back to its original state. For each of the three steps of the process, compute ΔU and ΔH . For each of the three steps, where possible, also calculate Q and W .
- *24.16 Two 1-m³ tanks submerged in a constant-temperature water bath of 77°C are connected by a globe valve. One tank contains steam at 40 kPa, while the second is completely evacuated. The valve is opened and the pressure in the two tanks equilibrates. Calculate:
- The work done in the expansion of the steam
 - The heat transferred to the tanks from the water bath
 - The change in internal energy of the combined steam system.
- ***24.17 One-tenth of a kg of steam at 650 K and 1000 kPa are enclosed in a metallic cylinder (mass 0.70 kg) by a piston (mass 0.46 kg) of area 118 cm². Both the piston and the cylinder have heat capacities of 0.34 J/(g of material)(K), and they are not insulated from the surroundings. The steam expands slowly pushing the piston up 80 cm where it is stopped and the pressure of the steam is 700 kPa. Find:
- The work done by the system of steam-piston-cylinder on the surroundings.
 - The final temperature of the steam.
 - The heat transfer between the system and the surroundings (state which way).
 - The change in volume of the steam in its expansion.
- *24.18 A household freezer is placed inside an insulated sealed room. If the freezer door is left open with the freezer operating, will the temperature of the room increase or decrease? Explain your answer.
- *24.19 Energy released by fruit and vegetables during cooling is called "heat of respiration." For potatoes the peak value is about 35 mW/kg at 5°C. Suppose that in an insulated storage room 52 pallets each containing 24 boxes of potatoes are stacked. Each box corresponds to 2.1 kg of cardboard and 20 kg of potatoes. The respective specific heats are 1.7 kJ/(kg)(°C) for the cardboard, and 3.05 kJ/(kg)(°C) for the potatoes.
- If the potatoes are cooled at the rate of 0.3 °C/hr, how much heat must be removed from the room in kW? Neglect the effect of air in the room.
- *24.20 For each process below, write down the general energy balance (include all terms). Based on the data given and any reasonable assumptions you make, simplify the balances as much as possible.
- A fluid flows through a tiny orifice from a region where its pressure is 1300 kPa and 600K to a pipe where the pressure is 275 kPa.
 - A turbine directly connected to an electric generator operates adiabatically. The working fluid enters the turbine at 250 psia and 600°F, and leaves at 50 psia and 400°F. The entrance and exit velocities of the fluid are negligible.
 - A fluid leaves the nozzle of a hose at 200 kPa and 400°C, and is brought to rest by passing it through the blades of an adiabatic turbine rotor. The fluid leaves the blades at 50 psia and 250°F.
- *24.21 A heating unit heats the air in a duct entering an auditorium by condensing saturated steam at 12 psia. The air (at 1 atm) is heated from 66°F to 76°F. Per 1000 ft³ of air en-

tering the heater, how many pounds of saturated steam must be condensed? The heating unit loses to the surroundings 3 Btu per pound of steam condensed.

- *24.22 Find the power output of an insulated generator that uses 700 kg/hr of steam at 10 atm and 500K. The steam exits at 1 atm and is saturated.
- *24.23 Water at 180°F is pumped at a rate of 100 ft³/hr through a heat exchanger to reduce the water temperature to 100°F. Find the rate at which heat is removed from the water in the heat exchanger.
- *24.24 In one system, carbon dioxide is flashed across an *insulated* throttling valve. The inlet pressure and temperature of the carbon dioxide are 1800 psia and 250°F, and the outlet of the valve is set at 60 psia. Indicate on the CO₂ chart the position of the inlet and outlet points as points A & B, respectively. What are: (a) the temperature, (b) the quality and (c) the specific volume of the outlet stream at 60 psia? Mark on the CO₂ chart as C an outlet state of 800 psia and 80°F. Mark as D on the chart an outlet state of 140 psia and -40°F. What is the quality of the CO₂ at state D?
- **24.25 A turbine is installed between the supply stream at 1800 psia and 250°F and the outlet stream. The exit stream from the turbine is at 800 psia and 80°F, and 25 Btu/lb of fluid are lost from the poorly insulated turbine. Indicate the outlet states from the turbine and the throttling valve as points on the CO₂ chart. See Figure P24.25
- How much useful work is extracted in the turbine?
 - The exhaust from the turbine enters a throttling valve and leaves at 140 psia and 30% liquid, but the valve is not perfectly insulated. What is the temperature of the exhaust stream at 140 psia?
 - How much heat is lost from the poorly insulated valve?

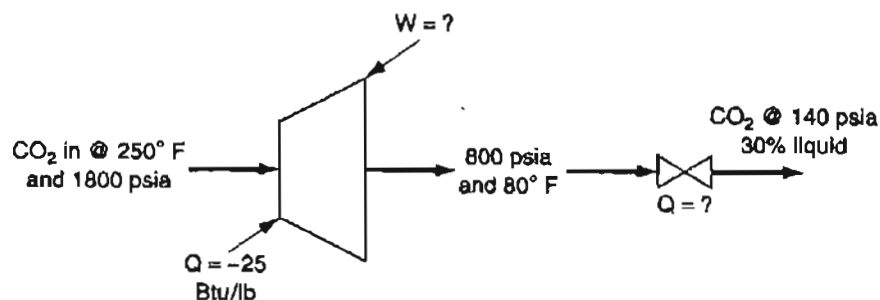


Figure P24.25

- *24.26 What is the heat that has to be transferred to a water heater of fixed volume to heat saturated water from 76°F to 220°F and 1 atm per pound of water?
- ✓ **24.27 In the vapor-recompression evaporator shown in Figure P24.27, the vapor produced on evaporation is compressed to a higher pressure and passed through the heating coil to provide the energy for evaporation. The steam entering the compressor is 98% vapor and 2% liquid, at 10 psia; the steam leaving the compressor is at 50 psia and 400°F; and 6 Btu of heat are lost from the compressor per pound of steam throughput. The condensate leaving the heating coil is at 50 psia, 200°F.
- Compute: The Btu of heat supplied for evaporation in the heating coil per Btu of work needed for compression by the compressor.
 - If 1,000,000 Btu per hour of heat is to be transferred in the evaporator, what must be the intake capacity of the compressor in ft³ of wet vapor per minute?

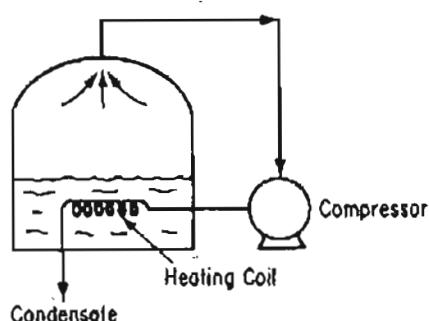


Figure P24.27

- *24.28** A 55-gal drum of fuel oil (15°API) is to be heated from 70°F to 180°F by means of an immersed steam coil. Steam is available at 220°F. How much steam is required if it leaves the coil as liquid water at 1 atm pressure? You can get the properties of the fuel oil from the CD accompanying this book.
- *24.29** Oil of average $C_p = 0.8 \text{ Btu/(lb)(°F)}$ flows at 2000 lb/min from an open reservoir standing on a hill 1000 ft high into another open reservoir at the bottom. To ensure rapid flow, heat is put into the pipe at the rate of 100,000 Btu/hr. What is the enthalpy change in the oil per pound? Suppose that a 1-hp pump (50% efficient) is added to the pipeline to assist in moving the oil. What is the enthalpy change per pound of the oil now?
- *24.30** Your company produces small power plants that generate electricity by expanding waste process steam in a turbine. One way to ensure good efficiency in turbine operation is to operate adiabatically. For one turbine, measurements showed that for 1000 lb/hr steam at the inlet conditions of 500°F and 250 psia, the work output from the turbine was 86.5 hp and the exit steam leaving the turbine was at 14.7 psia with 15% wetness (i.e., with a quality of 85%).

Check whether the turbine is operating adiabatically by calculating the value of Q . Also, calculate the ratio of the heat lost or gained to the enthalpy change across the turbine.

- **24.31** Feedwater heaters are used to increase the efficiency of steam power plants. A particular heater is used to preheat 10 kg/s of boiler feed water from 20°C to 188°C at a pressure of 1200 kPa by mixing it with saturated steam bled from a turbine at 1200 kPa and 188°C, as shown in Figure P24.31. Although insulated, the heater loses heat at the rate of 50 J per gram of exiting mixture. What fraction of the exit stream is steam?

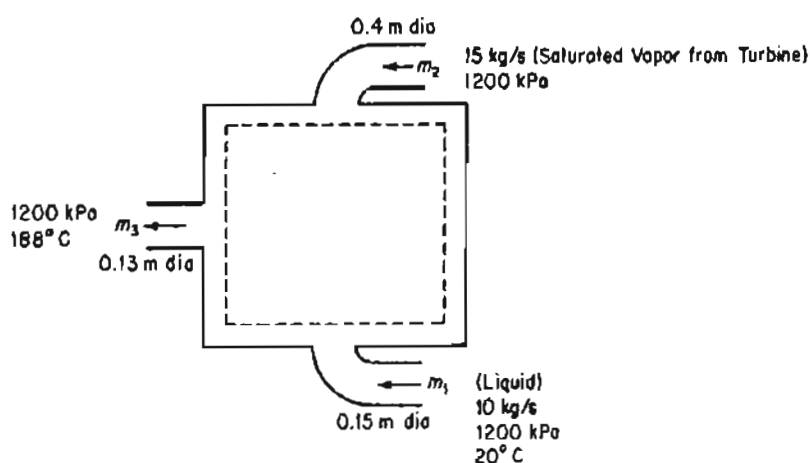


Figure P24.31

- **24.32** A family is planning to replace an electric water heater with a solar system. The specifications for the solar system are:

Water flow rate through the solar collection tubing: 1 gal/min

Inlet water temperature: 50°F

Outlet water temperature: 200°F

Tubing specifications: ASTM B241, 1.185 inch ID, 0.065 inch wall thickness

The tubes will be connected and placed in a glass covered box (to reduce heat loss) on the roof of the house forming a continuous series of U's. If solar energy is transferred to the tubes from 10 AM to 4 PM at the rate of 300 Btu/(hr)(ft of tubing), how many total feet of tubing will have to be purchased?

- *24.33** Three hundred kilograms per hour of air flow through a countercurrent heat exchanger as shown in Figure P24.33. Two hundred thirty kilograms per hour of potassium carbonate solution are heated by the air. Assume that the heat exchanger has negligible heat losses. The terminal temperatures are given in Figure P24.33. Calculate the temperature, in kelvin, of the exit potassium carbonate stream. Assume that the heat capacity of the potassium carbonate solution is the same as that of the water in the solution.

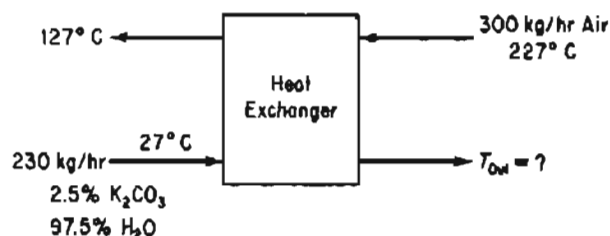


Figure P24.33

- ***24.34** A chemical plant has just perfected a process for the manufacturing of a new revolutionary drug. A large plant must be designed even before complete data are available. The research laboratory has obtained the following data for the drug.

boiling point at 101.3 kPa	250°C
vapor pressure at 230°C	55 kPa
specific gravity, 28°C/4°C	1.316
melting point	122.4°C
solubility in water at 76°C	2.2/100 parts water by weight
molecular weight	122
heat capacity of liquid	at 150°C is 2.09 kJ/(kg)(°C)
heat capacity of liquid	at 240°C is 2.13 kJ/(kg)(°C)

Calculate the heat duty for a vaporizer that will be required to vaporize 10,000 kg/hr of this chemical at atmospheric pressure (assume that no superheating of the vapor occurs). The entering temperature of the drug will be 130°C.

- ***24.35** A process involving catalytic dehydrogenation in the presence of hydrogen is known as *hydroforming*. Toluene, benzene, and other aromatic materials can be economi-

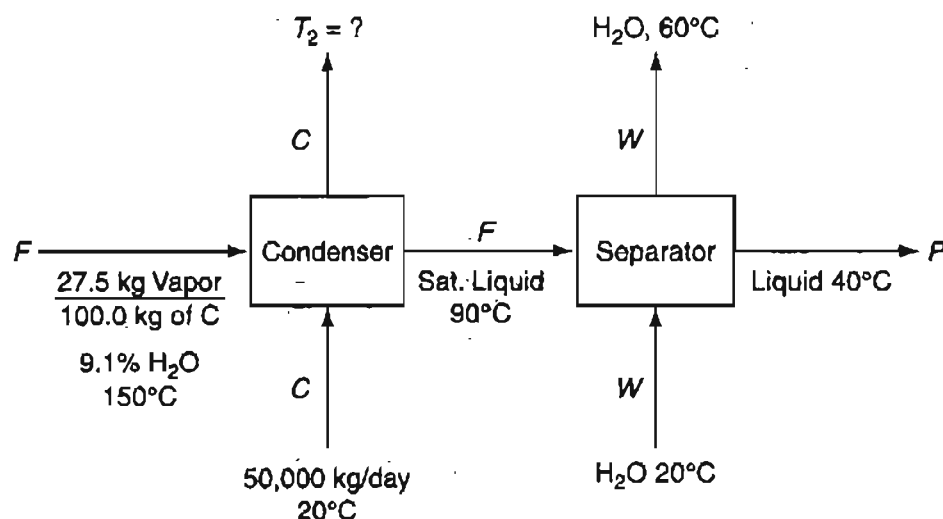


Figure P24.35

cally produced from naptha feed stocks in this way. After the toluene is separated from the other components, it is condensed and cooled in a process such as the one shown in Figure P24.35. For every 100 kg of C charged into the system, 27.5 kg of a vapor mixture of toluene and water (9.1% water) enter the condenser and are condensed by the C stream. Calculate:

- The temperature of the C stream after it leaves the condenser
- The kilograms of cooling water required per hour.

Additional data:

Stream	C_p [kJ/(kg)(°C)]	B.P. (°C)	ΔH_{vap} (kJ/kg)
H ₂ O(l)	4.2	100	2260
H ₂ O(g)	2.1	—	—
C ₇ H ₈ (l)	1.7	111	230
C ₇ H ₈ (g)	1.3	—	—
C(s)	2.1	—	—

✓***24.36 A power plant operates as shown in Figure P24.36. Assume that the pipes, boiler, and superheater are well lagged (insulated), and that friction can be neglected. Calculate (in Btu/lb steam):

- The heat supplied to the boiler
- The heat supplied to the superheater
- The heat removed in the condenser
- The work delivered by the turbine
- The work required by the liquid pumps

Also calculate the efficiency of the entire process defined as

$$\frac{\text{Net work delivered/lb steam}}{\text{Total heat supplied/lb steam}}$$

If the water rate to the boiler is 2000 lb/hr, what horsepower does the turbine develop?

Finally, what suggestion can you offer that will improve the efficiency of the power plant?

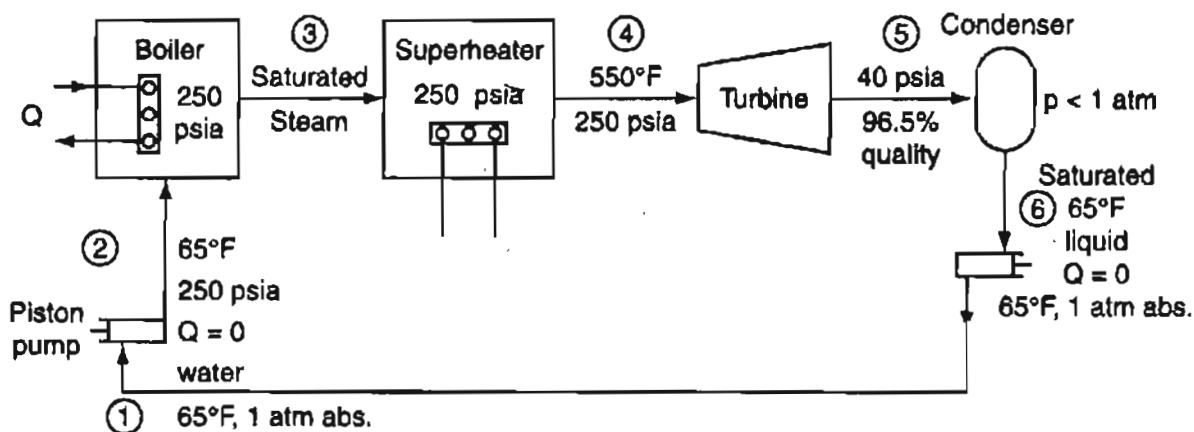


Figure P24.36

- ***24.37 A proposal to store Cl_2 as a liquid at atmospheric pressure was recently in the news. The operation is shown in Figure P24.37.

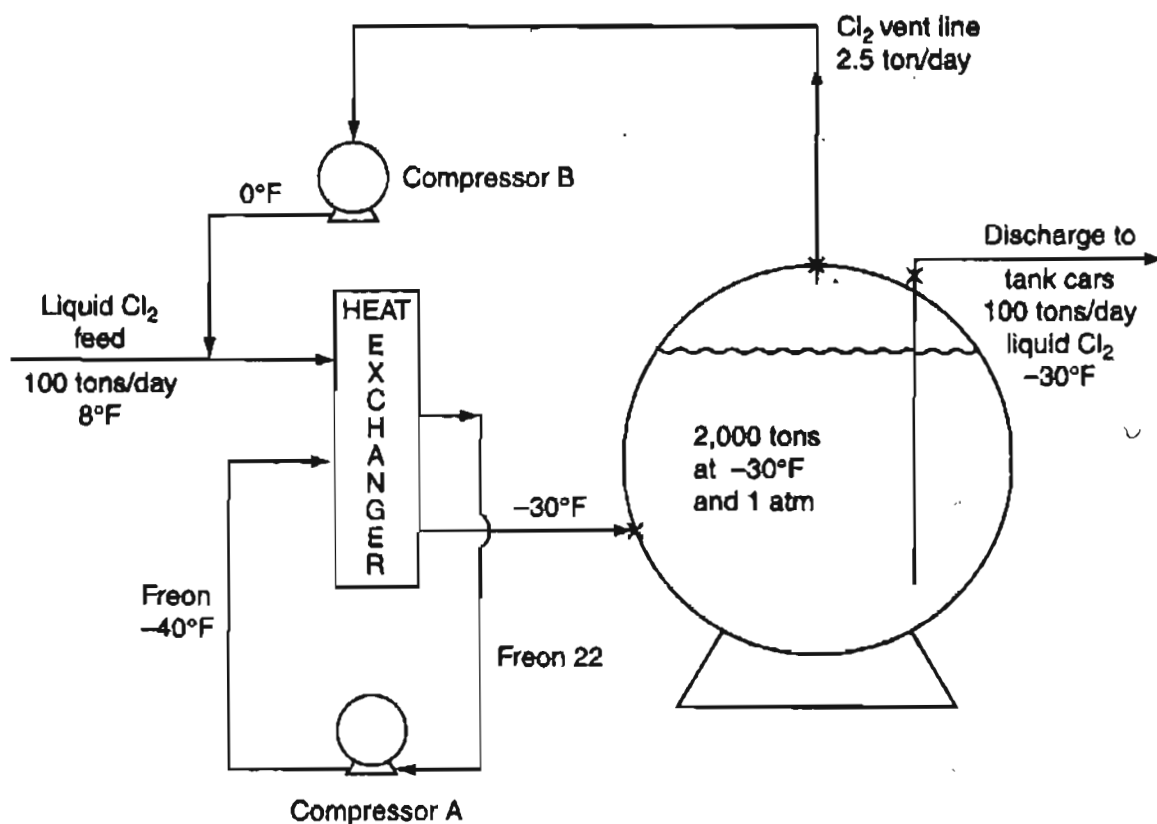


Figure P24.37

The normal boiling point of Cl_2 is -30°F . Vapor formed in the storage tank exits through the vent and is compressed to liquid at 0°F and returned to the feed. The vaporization rate is 2.5 tons/day when the sphere is filled to its capacity and the surrounding air temperature is 80°F .

If the compressors are driven by electric motors and are about 30% efficient, what is the hp input required to make this process successful? Assume lines and heat exchangers are well insulated. Use $8.1 \text{ Btu}/(\text{lb mol})(^\circ\text{F})$ for the heat capacity of liquid Cl_2 . $\Delta H_{\text{vaporization}} = 123.67 \text{ Btu}/\text{lb Cl}_2$.

- ***24.38 The initial process in most refineries is a simple distillation in which the crude oil is separated into various fractions. The flow sheet for one such process is illustrated in Fig. P24.38. Make a complete material and energy balance around the entire distillation system and for each unit including the heat exchangers and condensers. Also,

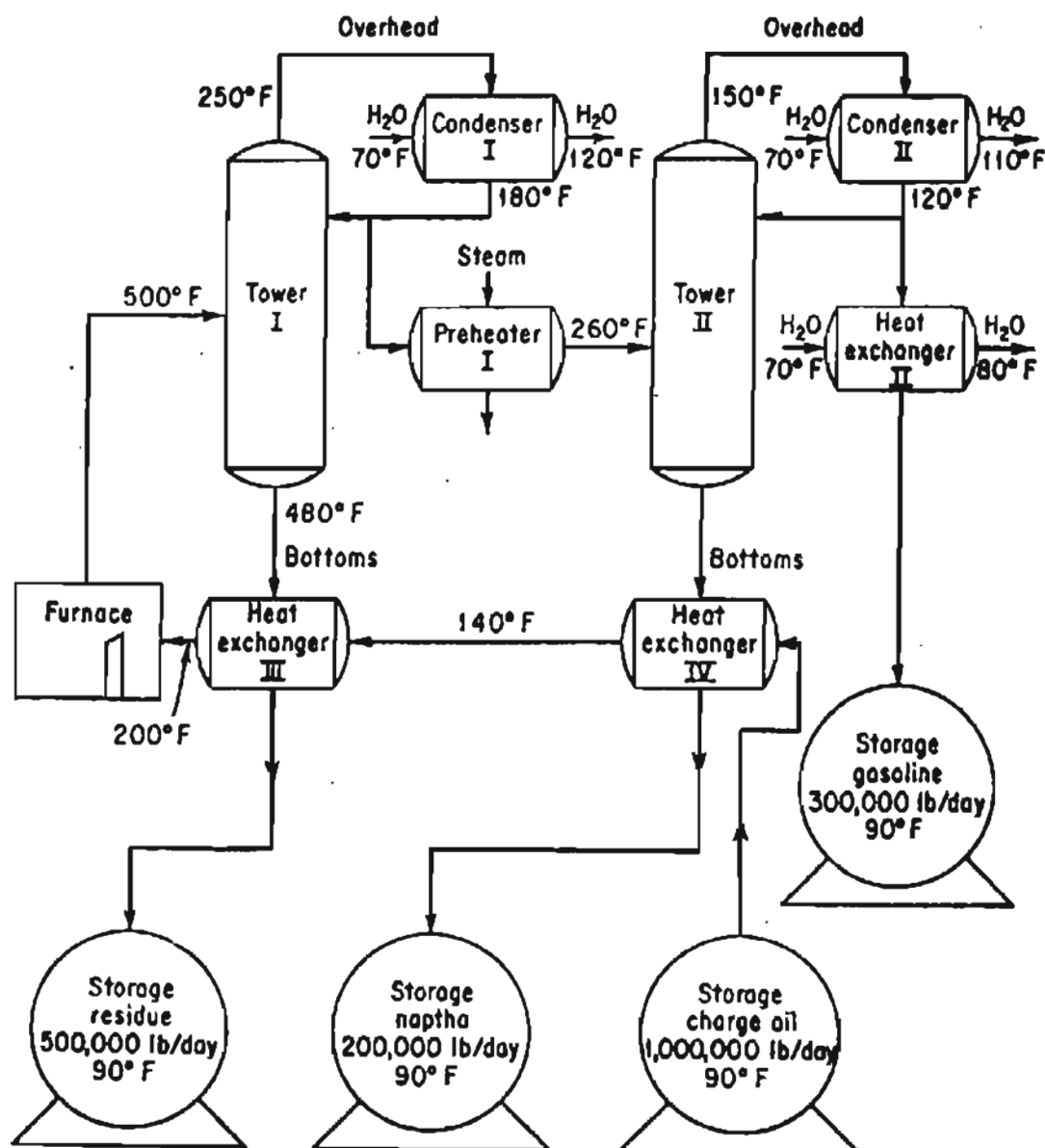


Figure P24.38

- (a) Calculate the heat load that has to be supplied by the furnace in Btu/hr.
 (b) Determine the additional heat that would have to be supplied by the furnace if the charge oil were not preheated to 200°F before it entered the furnace.

Do the calculated temperatures of the streams going into storage from the heat exchangers seem reasonable?

Additional data:

	Specific heat of liquid Btu/(lb)(°F)	Latent heat of vaporization Btu/lb	Specific heat of vapor Btu/(lb)(°F)	Condensation temp., °F
Charge oil	0.53	100	0.45	480
Overhead, tower I	0.59	111	0.51	250
Bottoms, tower I	0.51	92	0.42	500
Overhead, tower II	0.63	118	0.58	150
Bottoms, tower II	0.58	107	0.53	260

The reflux ratio of tower I is 3 recycle to 1 product.

The reflux ratio of tower II is 2 recycle to 1 product.

The reflux ratio is the ratio of the mass flow rate from the condenser to the mass flow rate that leaves the top of the tower (the overhead) and enters the condenser.

*****24.39** A boilerhouse flowsheet for a chemical process plant is shown in Figure P24.39. The production rate of 600 psia superheated steam is 100,000 lb/hr. The return condensate flowrate is 50,000 lb/hr. Calculate the:

- Flowrate of 30 psia steam required in the deaerator (lb/hr)
- Flowrate of make-up feed water (lb/hr)
- Pump horsepower (hp)
- Pump electrical consumption if the pump is 55% efficient (kW)
- Yearly electrical cost to operate the pump (at 0.05/kWh)
- Yearly electrical savings if the pump could be operated with a 600 psia discharge pressure.
- Heat input to the steam drum (Btu/hr)
- Heat input to the superheater section (Btu/hr)
- Amount of 30 psia steam lost to the atmosphere (lb/hr)
- Amount of 30 psia condensate lost to the atmosphere (lb/hr)

*****24.40** A distillation process has been set up to separate an ethylene-ethane mixture as shown in Fig. P24.40. The product stream will consist of 98% ethylene and it is desired to recover 97% of the ethylene in the feed. The feed, 1000 lb per hour of 35% ethylene, enters the preheater as a subcooled liquid (temperature = -100°F, pressure = 250 psia). The feed experiences a 20°F temperature rise before it enters the still. The heat capacity of liquid ethane may be considered to be constant and equal to 0.65 Btu/(lb)(°F) and the heat capacity of ethylene may be considered to be constant and equal to 0.55 Btu/(lb)(°F). Heat capacities and saturation temperatures of mixtures

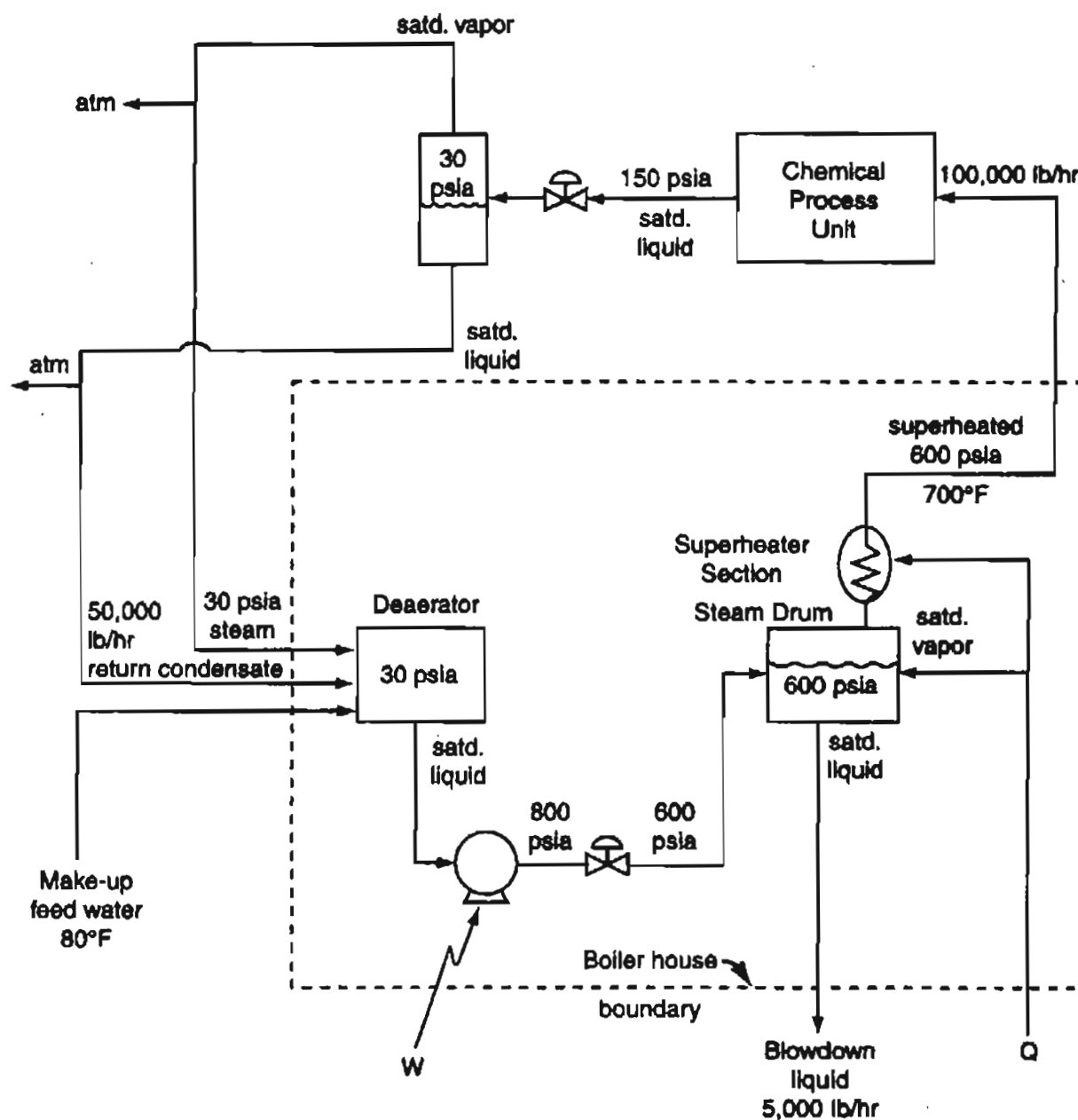


Figure P24.39

may be determined on a weight fraction basis. An optimum reflux ratio of 6.1 lb re-flux/lb product has been previously determined and will be used. Operating pressure in the still will be 250 psia. Additional data are as follows:

Pressure = 250 psia

Component	Temp. sat. (°F)	Heat of vaporization (Btu/lb)
C ₂ H ₆	10°	140
C ₂ H ₄	-30°	135

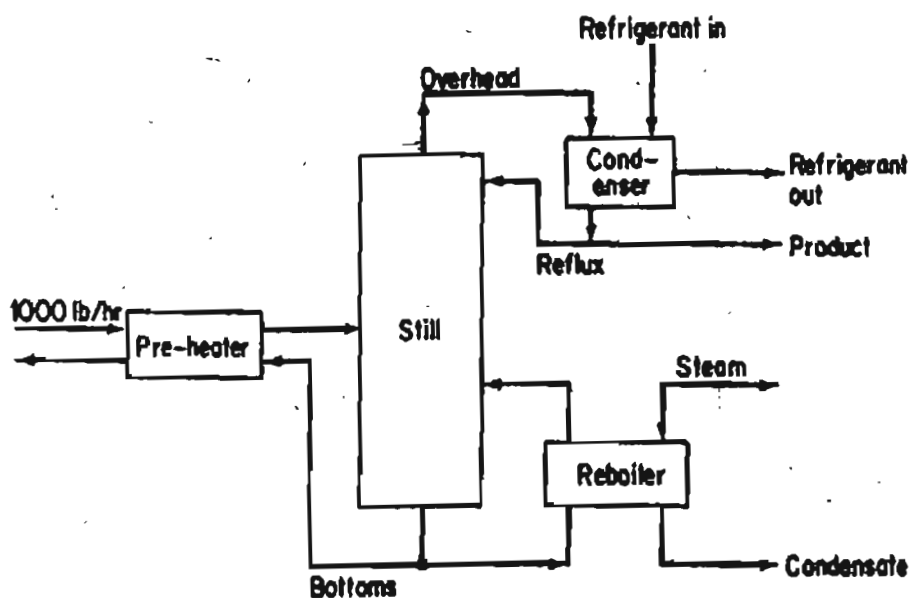


Figure P24.40

Determine:

- The pounds of 30 psig steam required in the reboiler per pound of feed.
- The gallons of refrigerant required in the condenser per hour assuming a 25°F rise in the temperature of the refrigerant. Heat capacity is approximately $1.0 \text{ Btu}/(\text{lb})(^{\circ}\text{F})$ and density $= 50 \text{ lb}/\text{ft}^3$.
- The temperature of the bottoms as it enters the preheater.

CHAPTER 25

ENERGY BALANCES: HOW TO ACCOUNT FOR CHEMICAL REACTION

25.1 The Standard Heat (Enthalpy) of Formation	764
25.2 The Heat (Enthalpy) of Reaction	769
25.3 Merging the Heat of Formation with the Sensible Heat of a Compound in Making an Energy Balance	780
25.4 The Heat of Combustion	785

Your objectives in studying this chapter are to be able to:

1. Explain the meaning of standard heat of formation, heat of reaction, and higher and lower heating values.
2. Compute the heats of formation from experimental data for a process in which a reaction is taking place.
3. Look up heats of formation in reference tables for a given compound.
4. List the standard conventions and reference states used for reactions associated with the standard heat of formation.
5. Calculate the standard heat of reaction from tabulated standard heats of formation for a given reaction.
6. Calculate the standard higher heating value from the lower heating value and vice versa.
7. Solve simple material and energy balance problems involving reactions.

As you probably are aware from our earlier comments, chemical reactions are at the heart of many industrial processes, and directly affect the economics of an entire plant. We have deferred including the effects of chemical reactions in the dis-

cussion of energy balances up to this point to avoid confusion. It's time to add them so that you can properly apply them to reacting systems.

Looking Ahead

In this chapter we focus on ways to include the effects of chemical reaction in the energy balance. We describe two closely related methods that treat the effects of energy generation or consumption somewhat differently. In one method, all of the energy effects are consolidated in one term in the energy balance. In the other, the energy effects are merged with the enthalpies associated with each stream flowing in and out of the system, and the material inside the system. Both methods involve a quantity known as the heat of formation, which we take up first.

25.1 The Standard Heat (Enthalpy) of Formation

As you probably know from chemistry, the observed heat transfer that occurs in an isothermal system in which a reaction takes place represents the energy change associated with the rearrangement of the bonds holding together the atoms of the reacting molecules. For an **exothermic reaction**, the energy required to hold the products of the reaction together is less than that required to hold the reactants together, and heat leaves the system. The reverse is true of an **endothermic reaction**. In this chapter we are concerned primarily with the enthalpy term in the steady-state energy balance for an open system, and to a lesser extent with the energy balance for a closed system.

To include energy changes caused by a reaction in the energy balance, we make use of a quantity called the **standard heat (really enthalpy) of formation**, often called just the heat of formation,* $\Delta \hat{H}_f^\circ$. The superscript $^\circ$ denotes the **standard state** for reaction of 25°C and 1 atm, and the subscript f denotes "formation."

The difficulty lies, not in the new ideas, but in escaping the old ones, which ramify, for those brought up as most of us have been, into every corner of our minds.

John Maynard Keynes

The standard heat of formation is the name given to the special enthalpy change associated with the formation of 1 mole of a compound from its con-

*Historically, the name arose because the changes in enthalpy associated with chemical reactions were generally determined in a device called a calorimeter, to which heat is added or removed from the reacting system so as to keep the temperature constant.

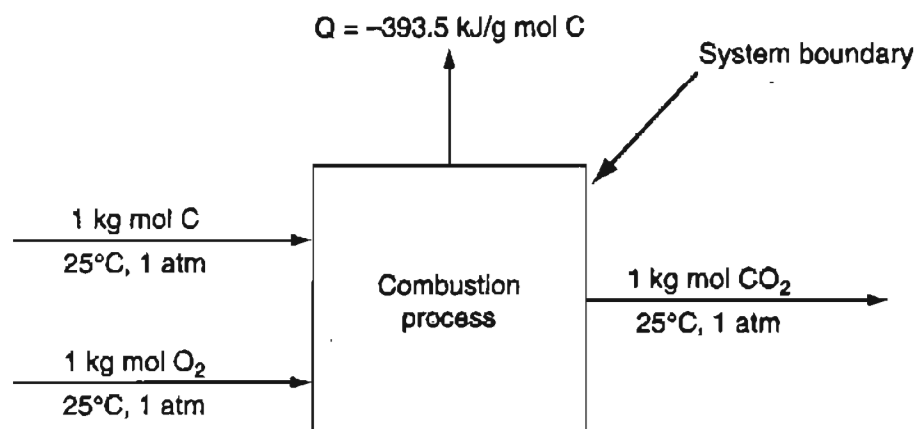
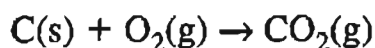


Figure 25.1 The heat transferred from a steady-state combustion process for the reaction $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ with reactants and products at 25°C and 1 atm.

stituent elements in their standard state. An example is the enthalpy change that occurs for the reaction of carbon and oxygen to form carbon dioxide at 25°C and 1 atm, as indicated in Figure 25.1



Note in the chemical reaction equation the explicit specification of the state of the compounds in parenthesis. For an energy balance applied to the process in Figure 25.1, $\Delta H = Q = -393.5 \text{ kJ/g mol of CO}_2$, and hence the standard heat of formation of CO_2 , is -393.5 kJ/g mol .

Since enthalpy is a state variable, any state would do for the standard state of reference, but, by convention, the standard state of a substance (both reactants and products) usually is 25°C and one atmosphere (absolute) pressure. Fixing a reference state should cause no problem because you are always interested in calculating *enthalpy differences* so that the reference state is eliminated.

The reaction does not necessarily represent a real reaction that would proceed at constant temperature, but can be a fictitious process for the formation of a compound from the elements. By defining **the heat of formation as zero in the standard state for each stable (e.g., N_2 vs. N) element**, it is possible to design a system to express the heats of formation for all *compounds* at 25°C and 1 atm. Appendix F is a short table of the standard heats of formation. On the CD in the back of this book you will find heats of formation for over 700 compounds, provided through the courtesy of Professor Yaws.* Remember that the values for the **standard heats of formation are negative for exothermic reactions**.

In the next example we show how to calculate the heats of formation from experimental data.

*Yaws, C. L. "Correlation Constants for Chemical Compounds," *Chem. Engr.*, **79** (August 15, 1976).

EXAMPLE 25.1 Determination of a Heat of Formation from Heat Transfer Measurements

Suppose that you want to find the standard heat of formation of CO from experimental data. Can you prepare pure CO from the reaction of C and O₂, and measure the heat transfer? This would be far too difficult. It would be easier experimentally to find first the heat of reaction at standard conditions for the two reactions shown below for the flow process as shown in Figure E25.1.

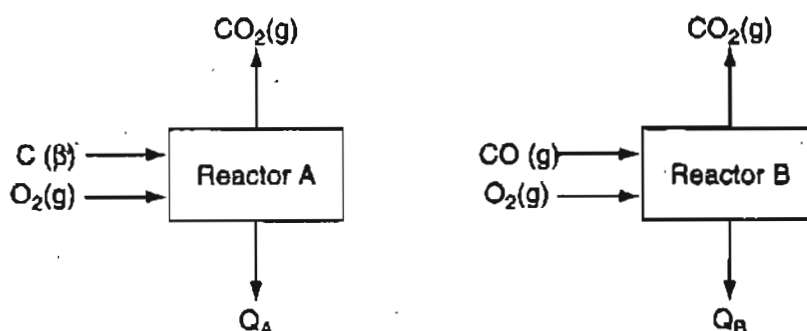
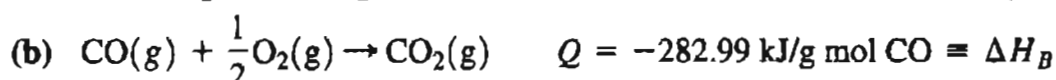
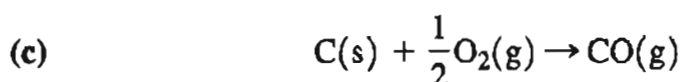


Figure E25.1 Use of two convenient reactions to determine the heat of formation for an inconvenient reaction $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$.



Basis: 1 g mol of C and CO

According to Hess's Law, you subtract reaction (b) from reaction (a), subtract the corresponding ΔH 's, and rearrange the compounds to form the desired chemical equation



for which the net heat of reaction per g mol CO is the heat of formation of CO

$$\Delta H_f^\circ = -393.51 - (-282.99) = -110.52 \text{ kJ/g mol C}$$

One hazard assessment of a compound is based on the potential rapid release of energy. A common prediction method of such release is to use the heat of formation per gram of compound as a guide. For example, what would you predict about the relative hazard of the following compounds: acetylene gas, lead azide solid, trinitro glycerine (TNT) liquid, and ammonium nitrate solid? Would you pick TNT

as the most explosive? If so, you would be wrong. Check the respective heats of formation in Appendix F and convert to a per gram basis.

Most likely you will obtain values for the heats of formation from reference tables or databases prepared from experimental data as illustrated in the next example.

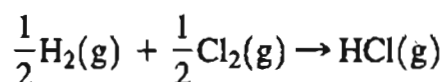
EXAMPLE 25.2 Retrieval of Heats of Formation from Reference Data

What is the standard heat of formation of HCl(g) ?

Solution

Look in Appendix F. The column heading is $\Delta \hat{H}_f^\circ$, and in the column opposite HCl(g) read -92.311 kJ/g mol .

In the reaction to form HCl(g) at 25°C and 1 atm



Both $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ are assigned $\Delta \hat{H}_f^\circ$ values of 0, and consequently the value shown in Appendix F for HCl(g) of -92.311 kJ/g mol is the standard heat of formation for this compound

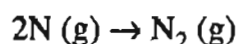
$$\Delta H_f^\circ = 1(-92.311) - \left[\frac{1}{2}(0) + \frac{1}{2}(0) \right] = -92.311 \text{ kJ/g mol HCl(g)}$$

The value tabulated in Appendix F might actually be determined by carrying out the reaction shown for HCl(g) and measuring the heat transfer from a calorimeter, or by some other more convenient method.

SELF-ASSESSMENT TEST

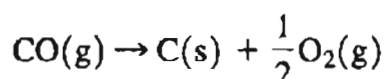
Questions

1. If for the reaction



the heat transfer is $Q = -941 \text{ kJ}$, how do you determine the value for the heat of formation of $\text{N}_2(\text{g})$?

2. If the reaction for the decomposition of CO

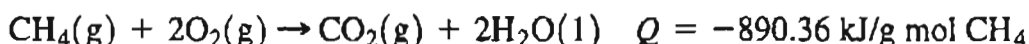


takes place only at high temperature and pressure, how will the value of the standard heat of formation of CO be affected?

- Will reversing the direction of a reaction equation reverse the sign of the heat of formation of a compound?

Problems

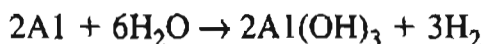
- What is the standard heat of formation of HBr (g)?
- Show that for the process in Figure 25.1 the general energy balance reduces to $Q = \Delta H$. What assumptions do you have to make?
- Could the heat of formation be calculated from measurements taken in a batch process? If so, show the assumptions and calculations.
- Calculate the standard heat of formation of CH₄ given the following experimental results at 25°C and 1 atm (Q is for complete reaction):



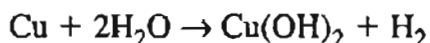
Compare your answer with the value found in the table of the heats of formation listed in Appendix F.

Thought Problems

- Mercury is known to amalgamate with many metals—the recovery of gold in ancient times is well known. Normally water does not react with the aluminum in tubes in which water flows because the thin film of aluminum oxide that adheres to the aluminum surface prevents additional reaction from taking place. However, mercury contamination prevents the oxide film from functioning as a protector of the aluminum, and the aluminum readily corrodes by the reaction at room temperature



You might expect copper tubes to also be attacked by water with an amalgam present by the reaction



but copper is not corroded. Why? Hint: The film is not protective for Cu-Hg amalgam.

- Why are conventional automobiles undrivable using a pure methanol or ethanol fuel?
- A review of additives to gasoline to give blends that improve its octane rating shows that oxygenated compounds necessarily contain lower energy (Btu per gallon). Methanol was the lowest, having a heat of reaction approximately one-half that of gasoline. Methanol without tax costs 40 cents/gal, whereas unleaded premium gas costs 80 cents/gal, so that

the result may seem like a standoff (i.e., half the energy at half the cost). Are the two fuels really equivalent in practical use?

Discussion Problem

1. Many different opinions have been expressed as to whether gasohol is a feasible fuel for motor vehicles. An important economic question is: Does 10% grain-based-alcohol-in-gasoline gasohol produce positive net energy? Examine the details of the energy inputs and outputs, including agriculture (transport, fertilizer, etc.), ethanol processing (fermentation, distilling, drying, etc.), petroleum processing and distribution, and the use of by-products (corn cobs, stalks, mash, etc.). Ignore taxes and tax credits, and assume that economical processing takes place. Discuss octane ratings, heats of vaporization, flame temperatures, fuel to air ratios, volumetric fuel economy, effect of added water, and the effect on engine parts.

25.2 The Heat (Enthalpy) of Reaction

What is the difference between a method and a device?

A method is a device which you use twice.

George Polya

As we mentioned previously, one method of including the effect of chemical reaction in the energy balance uses the heat of reaction. The **heat of reaction** (that should be but is only rarely called the **enthalpy of reaction**) is the enthalpy change that occurs when *stoichiometric quantities* of reactants at some T and p react to form products at the *same* T and p . The **standard heat of reaction** ($\Delta \hat{H}_{\text{rxn}}^\circ$) is the name given to the heat of reaction (enthalpy change) for one mole of a compound that reacts at 25°C and 1 atm^* (the standard state for reaction) when stoichiometric quantities of reactants in the standard state **react completely** to produce products in the standard state. Don't confuse the symbol for the standard heat of reaction, $\Delta \hat{H}_{\text{rxn}}^\circ$, for one mole with the more general heat of reaction symbol, ΔH_{rxn} , which can apply to more or less than 1 mole. If the reaction is not at 25°C and 1 atm , the superscript $^\circ$ is deleted. In your calculations, you usually base the heat of reaction on a chemical reaction equation.

You can obtain the heat of reaction from experiments of course, but it is easier to calculate the standard heat of reaction from the tabulated values of the heats of formation as follows. Consider a steady-state flow process with no work involved, such as shown in Figure 25.2 in which benzene (C_6H_6) reacts with the stoichiometric amount of H_2 to produce cyclohexane (C_6H_{12}) in the standard state:

*The standard pressure is 1 bar (100 kPa) in some tabulations.

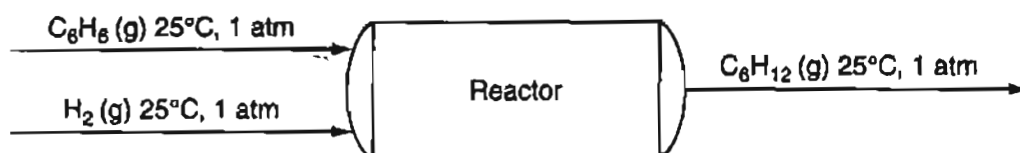
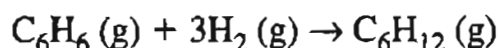


Figure 25.2 Reaction of benzene to form cyclohexane.



The energy balance for the process reduces to $Q = \Delta H$ where ΔH is by definition $\Delta \hat{H}_{\text{rxn}}^0$ for the specified chemical reaction equation.

Because we adopt for the heat of reaction the same reference conditions (0 enthalpy for the elements at 25°C and 1 atm) as used in defining the heats of formation, the values of the enthalpies associated with each species involved in the reaction are just the values of the respective heats of formation. For the process shown in Figure 25.2, the data are

Compound	Specific Enthalpy = $\Delta \hat{H}_f^0$ (kJ/g mol)
$\text{C}_6\text{H}_6 (\text{g})$	82.927
$\text{H}_2 (\text{g})$	0
$\text{C}_6\text{H}_{12} (\text{g})$	-123.1

You calculate the standard heat of reaction thus:

$$\begin{aligned} \Delta \hat{H}_{\text{rxn}}^0 &= \nu_{\text{C}_6\text{H}_{12}} \Delta \hat{H}_{f, \text{C}_6\text{H}_{12}}^0 - \nu_{\text{C}_6\text{H}_6} \Delta \hat{H}_{f, \text{C}_6\text{H}_6}^0 - \nu_{\text{H}_2} \Delta \hat{H}_{f, \text{H}_2}^0 \\ &= (1)(-123.1) - (1)(82.927) - (3)(0) = -206.0 \text{ kJ} \end{aligned}$$

The $\Delta \hat{H}_{\text{rxn}}^0$ is for the reaction as written, and actually has the units of energy per moles reacting for the specified chemical equation.

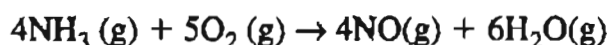
In general for complete reaction

$$\Delta \hat{H}_{\text{rxn}}^0(25^\circ\text{C}) = \left(\sum_i^{\text{Products}} \nu_i \Delta \hat{H}_{f,i}^0 - \sum_i^{\text{Reactants}} \nu_i \Delta \hat{H}_{f,i}^0 \right) \quad (25.1)$$

Keep in mind that the “heat of reaction” is actually an **enthalpy change**, and not necessarily equivalent to heat transfer to or from the system. If you do not have values for the heats of formation, you can estimate them as described in some of the references listed at the end of this chapter. If the stoichiometry of the reaction is not well known, you may have to carry out an experiment to get the heat of reaction.

EXAMPLE 25.3 Calculation of the Standard Heat of Reaction from the Standard Heats of Formation

Calculate $\hat{H}_{\text{rxn}}^{\circ}$ for the following reaction of 4 g mol of NH_3 :

**Solution**

Basis: 4 g mol of NH_3

<i>Tabulated data</i>	<u>$\text{NH}_3(\text{g})$</u>	<u>$\text{O}_2(\text{g})$</u>	<u>$\text{NO}(\text{g})$</u>	<u>$\text{H}_2\text{O}(\text{g})$</u>
$\Delta H_{\text{rxn}}^{\circ}$ per mole at 25°C and 1 atm (kJ/g mol)	-46.191	0	+90.374	-241.826

We shall use Equation (25.1) to calculate $\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}(25^{\circ}\text{C})$ for 4 g mol of NH_3 assuming complete reaction:

$$\begin{aligned}\Delta H_{\text{rxn}}(25^{\circ}\text{C}) &= [4(90.374) + 6(-241.826)] - [5(0) + 4(-46.191)] \\ &= -904.696 \text{ kJ/4 g mol NH}_3.\end{aligned}$$

Per g mol of reaction $\Delta \hat{H}_{\text{rxn}}^{\circ} = -226.174 \text{ kJ/g mol NH}_3$.

So far we have focused on the heat of reaction for complete reaction. What if the reaction is not complete? As discussed in Chapters 9 and 10, for most processes the moles of reactants entering are not in their stoichiometric quantities, and the reaction may not go to completion so that some reactants appear in the product from the reactor. How do you then calculate the heat of reaction, $\Delta H_{\text{rxn}}(25^{\circ}\text{C})$ (not the standard heat of reaction), in the standard state? One way is to start with Equation (25.1), and use the extent of reaction if you know it or can calculate it. For each species associated with the reaction for a batch system

$$n_i^{\text{final}} = n_i^{\text{initial}} + v_i \xi$$

or the equivalent for a flow system

$$n_i^{\text{out}} = n_i^{\text{in}} + v_i \xi$$

Thus

$$\Delta H_{\text{rxn}}(25^{\circ}\text{C}) = \sum_i^{\text{Products}} (n_i^{\text{in}} + v_i \xi) \Delta \hat{H}_{f,i}^{\circ} - \sum_i^{\text{Reactants}} (n_i^{\text{in}}) \Delta \hat{H}_{f,i}^{\circ}$$

You can change the summations to sum over all the species associated with the reaction if you let $n_i = 0$ for any species not present as a product or reactant

$$\begin{aligned}\Delta H_{\text{rxn}}(25^\circ\text{C}) &= \sum n_i^{\text{in}} \Delta \hat{H}_{f,i}^\circ + \sum v_i \xi \Delta \hat{H}_{f,i}^\circ - \sum n_i^{\text{in}} \Delta \hat{H}_{f,i}^\circ \\ &= \xi \sum_{\text{all species}} v_i \Delta \hat{H}_{f,i}^\circ = \xi \Delta H_{\text{rxn}}^\circ\end{aligned}\quad (25.2)$$

For example, for the reaction in Figure 25.2, assume the fraction conversion is 0.80. Then, based on the limiting reactant C_6H_{12} ,

$$\xi = \frac{-(0.80)(1)}{-1} = 0.80$$

$$\Delta H_{\text{rxn}}(25^\circ\text{C}) = (0.80)[(1)(-123.1) + (-3)(0) + (-1)(82.927)] = -164.8 \text{ kJ}$$

Can you calculate the heat of reaction for a process in which the reactants enter and products exit at a common temperature other than 25°C and 1 atm? The answer is yes. Recall that enthalpy is a state (point) variable. Then you can calculate a change in enthalpy by any path that goes from the initial state to the final state.

Look at Figure 25.3. We want to calculate the $\Delta H_{\text{rxn}}(T)$ (enthalpy change [heat of reaction] from state 1 to 2 at T). The value is the same as summing the value of all the enthalpy changes 1 to 3, 3 to 4, and 4 to 2. The enthalpy change $H(T) - H(25^\circ\text{C})$ for the reactants and products is the combination of the sensible and latent heat (enthalpy) changes that might be taken from a table, or be calculated for one species as follows:

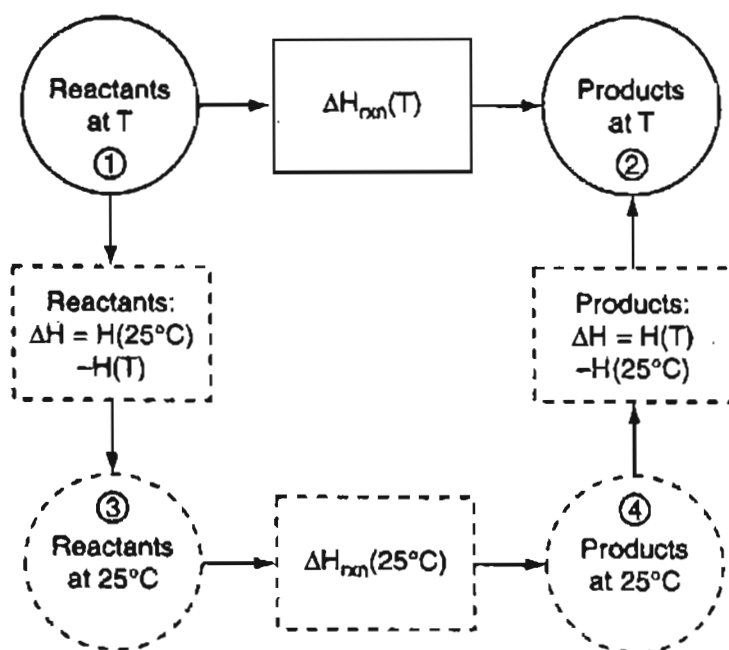


Figure 25.3 Information used in calculating the enthalpies comprising $\Delta H_{\text{rxn}}(T)$.

$$H_i(T) - H_i(25^\circ\text{C}) = n_i \int_{25^\circ\text{C}}^T C_{p,i} dT + n_i \Delta \hat{H}_{i, \text{phase change}} \quad (25.3)$$

In summary, ignoring any slight pressure and mixing effects, the heat of reaction at a temperature other than the reference temperature is

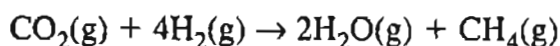
$$\Delta H_{\text{rxn}}(T) = \sum_i^{\text{Reactants}} n_i [\hat{H}_i(25^\circ\text{C}) - \hat{H}_i(T)] + \Delta H_{\text{rxn}}(25^\circ\text{C}) \quad (25.4)$$

$$+ \sum_i^{\text{Products}} n_i [\hat{H}_i(T) - \hat{H}_i(25^\circ\text{C})]$$

$$= [H(T) - H(25^\circ\text{C})]_{\text{Products}} - [H(T) - H(25^\circ\text{C})]_{\text{Reactants}} + \Delta H_{\text{rxn}}(25^\circ\text{C}) \quad (25.4a)$$

EXAMPLE 25.4 Calculation of the Heat of Reaction at a Temperature Different from the Standard Conditions

Public concern about the increase in the carbon dioxide in the atmosphere has led to numerous proposals to sequester or eliminate the carbon dioxide. An inventor believes he has developed a new catalyst that can make the gas phase reaction



proceed with 100% conversion of CO_2 . The source of the hydrogen would be from the electrolysis of water using electricity generated from solar cells. Assume stoichiometric amounts of the reactants enter the reactor. Determine the heat of reaction if the gases enter and leave at 1 atm and 500°C .

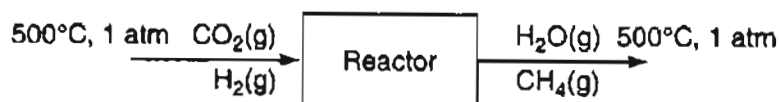


Figure E25.4

Solution

Basis: 1 g mol CO_2 (g) at 500°C and 1 atm

To avoid errors, the sensible heat data below in the fourth column have been taken from the CD in the back of this book instead of integrating the respective heat capacity equations by hand. Complete reaction is specified.

A convenient and compact way of making the calculations is to set up a table to display the data:

Compounds	g mol	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	$\Delta \hat{H}_{25^\circ\text{C}}^{500^\circ\text{C}}$ (kJ/g mol)
CO ₂ (g)	1	-393.250	21.425
H ₂ (g)	4	0	13.834
H ₂ O(g)	2	-241.835	17.010
CH ₄ (g)	1	-74.848	23.126

$\Delta H_{\text{rxn}}(25^\circ\text{C}) = [(1)(-74.848) + 2(-241.835)] - [(1)(-393.250) + 4(0)] = -165.27 \text{ kJ}$

Reactants
 $\sum_i [H_i(500^\circ\text{C}) - H_i(25^\circ\text{C})] = (1)(21.425) + (4)(13.834) = 76.761$

Products
 $\sum_i [H_i(500^\circ\text{C}) - H_i(25^\circ\text{C})] = (2)(17.010) + (1)(23.126) = 57.146$

$\Delta H_{\text{rxn}}(500^\circ\text{C}) = 57.146 - 76.761 + (-165.27) = -184.9 \text{ kJ}$

Next, let's look at how the heat of reaction fits into the general energy balance $\Delta E = Q + W - \Delta H - \Delta PE - \Delta KE$.

In the energy balance the enthalpy change for the compounds involved in the reaction is (refer back to Figure 25.3)

$$\begin{aligned} \Delta H = & [H(25^\circ\text{C}) - H(T^{\text{in}})]_{\text{Reactants}} + \Delta H_{\text{rxn}}(25^\circ\text{C}) \\ & + [H(T^{\text{out}}) - H(25^\circ\text{C})]_{\text{Products}} \end{aligned} \quad (25.5)$$

Because of the selection of the reference temperature, $\Delta H(25^\circ\text{C}) = 0$ for both reactants and products

$$\Delta H = H_{\text{Products}}(T^{\text{out}}) - H_{\text{Reactants}}(T^{\text{in}}) + \Delta H_{\text{rxn}}(25^\circ\text{C}) \quad (25.6)$$

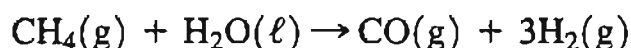
Any compounds not involved in the reaction (such as N₂, for example, in combustion) can be included in the first two terms on the righthand side of the equal sign in Equation (25.6), but they make no contribution to the heat of reaction at 25°C. Then Equation (25.6) becomes

$$\Delta H = [H(T^{\text{Outputs}})]_{\text{Outputs}} - [H(T^{\text{Inputs}})]_{\text{Inputs}} + \Delta H_{\text{rxn}}(25^\circ\text{C}) \quad (25.6a)$$

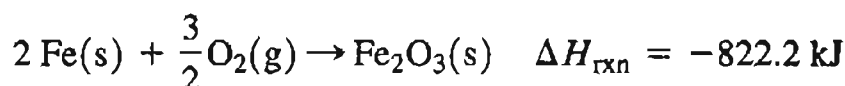
The conclusion that you should reach from Equation (25.6a) is that when reaction occurs in a system, just one term has to be added to the energy balance, namely the heat of reaction at 25°C. All of the effects of energy generation or consumption caused by reaction can be lumped into the one quantity $\Delta H_{\text{rxn}}(25^\circ\text{C})$. Chapter 26 illustrated the application of the general energy balance when $\Delta H_{\text{rxn}}(25^\circ\text{C})$ is involved.

You have to be a bit careful in using the heat of reaction to get ΔH for an energy balance because certain conventions exist:

- a. The reactants are shown on the lefthand side of the chemical equation, and the products are shown on the right, for example,



- b. The conditions of phase, temperature, and pressure must be specified unless the last two are standard conditions, as presumed in the equation above, when only the phase is required. This is particularly important for a compound such as H_2O , which can exist as more than one phase under common conditions.
- c. The amounts of material reacting are assumed to be the quantities shown by the stoichiometry in the chemical equation. Thus, if the reaction is



the value of -822.2 kJ refers to 2 g mol of $\text{Fe}(\text{s})$ reacting and not 1 g mol. The heat of reaction for 1 g mol of $\text{Fe}(\text{s})$ would be $-411.1 \text{ kJ/g mol Fe}$.

EXAMPLE 25.5 Calculation of the Heat Transfer Using the Heat of Reaction in a Process in which the Reactants Enter and the Products Leave at Different Temperatures

A test of the process described in Example 25.4 showed on the basis of 1 g mol of CO_2 entering from another process at 800 K, and reacting with 4 g mol H_2 entering at 298 K, that only 70% conversion of the CO_2 occurred. The products exited from the reactor at 1000 K. Calculate the heat transfer to or from the reactor for the test.

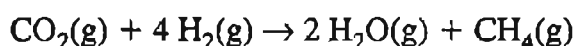
Solution

The system is steady state and open with reaction. Assume 1 atm.

Basis: 1 g mol of $\text{CO}_2(\text{g})$

The reference temperature is 25°C .

The first step is to calculate the heat of reaction at the reference temperature. The reaction is



$$\Delta \hat{H}_{\text{rxn}}^\circ = [(1)(-74.84) + (2)(-241.835)] - [(1)(-393.51) + (4)(0)] = -165.27 \text{ kJ}$$

For 70% conversion of the CO_2

$$\Delta H_{\text{rxn}}(25^\circ\text{C}) = (0.70)(-165.27) = -115.69 \text{ kJ}$$

The next step is to calculate the enthalpy changes from 298K to the respective temperatures of the compounds entering and leaving the reactor. The material balance results are listed in column 2 of the table below.

Comp.	g mol	T(K)	Sensible heat $\Delta \hat{H}_{298}^T$ (kJ/g mol)	Total enthalpy ΔH_{298}^T (kJ)
<i>In</i>				
CO ₂ (g)	1	800	22.798	22.798
H ₂ (g)	4	298	0	0
			Total	22.798
<i>Out</i>				
H ₂ (g)	1.2	1000	20.620	24.744
CH ₄ (g)	0.7	1000	38.325	26.828
CO ₂ (g)	0.3	1000	33.396	10.019
H ₂ O(l)	1.4	1000	25.986	36.380
			Total	97.971

The energy balance reduces to $Q = \Delta H$.

$$Q = \Delta H = 97.971 - 22.798 + (-115.69) = -40.517 \text{ kJ/g mol CO}_2$$

EXAMPLE 25.6 Calculation of the Enthalpy Change in an Anerobic Culture

An anerobic (in the absence of air) culture of *Lacto bacillus casei* used mannitol as the energy source for the production of ethanol, acetate, formate, and lactate compounds. The values of the enthalpy changes for each compound in the solution were calculated from estimates of the oxidation of each metabolite:

	ΔH (kJ/g mol)	g mol produced/g mol mannitol
Ethanol	-1330.51	1.29
Acetate	-887.01	0.22
Formate	-221.75	1.6
Lactate	-1330.51	0.4
Mannitol	-2882.78	1.0 (consumed)

The biomass growth was 40.5 g cells/g mol mannitol. Calculate the net enthalpy change for the several products (metabolites) per (a) g mol mannitol consumed and (b) g cells produced.

Solution

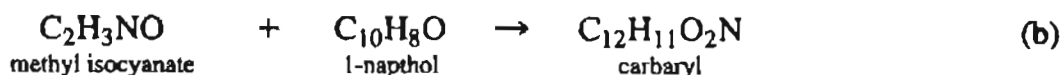
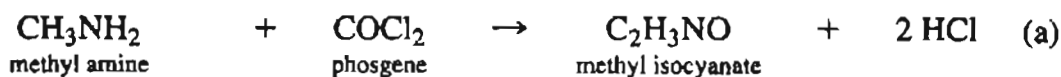
Basis: 1 g mol of mannitol reacting

$$\Delta H = [1.29(-1330.51) + 0.22(-887.01) + 1.6(-221.75) + 0.4(-1330.51)] - 1.0(-2882.78) = -84.28 \text{ kJ/g mol mannitol}$$

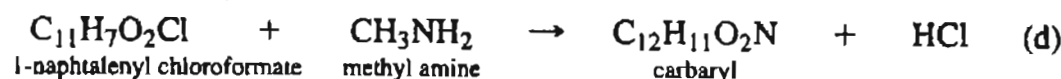
$$\text{Per gram of cells: } \Delta H = \frac{-84.28 \text{ kJ}}{1 \text{ g mol mannitol}} \left| \frac{1 \text{ g mol mannitol}}{40.5 \text{ g cells}} \right| = 2.08 \text{ kJ/g cells}$$

EXAMPLE 25.7 Green Chemistry: Examining Alternate Processes

Green chemistry refers to the adoption of chemicals in commercial processes that cause less concern in the environment. An example is the elimination of methyl isocyanate, a very toxic gas, in the production of carbaryl (1-naphthalenyl methyl carbamate). In 1984 in Bhopal, India, the accidental release of methyl isocyanate in a residential area led to the death of thousands of people and the injury of many more. The Bhopal process can be represented by the reaction equations (a) and (b):



An alternate process eliminating the methyl isocyanate is represented by two different reaction equations:



All of the reactions are in the gas phase. Calculate the major amount of heat transfer that will be required in each step of each process per g mol of carbaryl produced overall in the process. Will there be any additional cost of heat transfer using the greener process?

Data: Note, some of the values listed are only estimates. All of the values for the $\Delta \hat{H}_f^\circ$ are in kJ/g mol.

Component	$\Delta \hat{H}_{\text{rxn}}^\circ$ kJ/gmol
Carbaryl	-26
Hydrogen chloride	-92.311
Methyl amine	-20.0
Methyl isocyanate	-9.0×10^4
1-Naphthalenyl chloroformate	-17.9
1-Naphthol	30.9
Phosgene	-221.85

Solution

Basis: 1 g mol carbaryl

The simplest analysis is to say $\Delta H_{\text{rxn}}^0 = Q$ so that the values of the standard heats of reaction will be the measure of the major contributions to the energy balances for the respective processes.

$$\text{Reaction (a): } \Delta H_{\text{rxn}}^0 = [2(-92.311) + 1(-90,000)] - [1(-20.0) + 1(-221.85)] = -9.0 \times 10^4 \text{ kJ}$$

$$\text{Reaction (b): } \Delta H_{\text{rxn}}^0 = [1(-26)] - [1(-90,000) + 1(30.9)] = \frac{9.0 \times 10^4 \text{ kJ}}{\text{Total} \approx 0 \text{ kJ}}$$

$$\text{Reaction (c): } \Delta H_{\text{rxn}}^0 = [1(-17.9)] - [1(30.9) + 1(-221.85)] = 173.05$$

$$\text{Reaction (d): } \Delta H_{\text{rxn}}^0 = [1(-26) + 1(-92.311)] - [1(-17.9) + 1(-20.0)] = \frac{-80.41 \text{ kJ}}{\text{Total} \approx 92 \text{ kJ}}$$

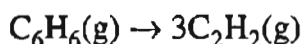
The original process and the final process both require relatively small heat removal overall, but the Bhopal process requires considerable heat transfer on each of the two stages of the process, with stage (a) requiring removal and stage (b) requiring heating. The capital costs of the Bhopal process could be higher than the alternate process.

SELF-ASSESSMENT TEST**Questions**

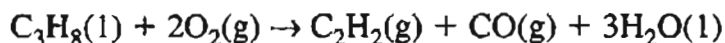
1. Can the standard heat of reaction ever be positive?
2. Is it correct to calculate a heat of reaction for a process in which the reaction is incomplete?
3. How does phase change, such as when water goes from a liquid to a vapor, affect the value of the heat of reaction?
4. What does it mean when the standard heat of reaction is (a) negative and (b) positive?
5. Can you choose a reference state other than 25°C and 1 atm to use in applying the energy balance?
6. What is the difference between the heat of reaction and the standard heat of reaction?

Problems

1. Calculate the standard heat of reaction for the following reaction from the heats of formation:



2. Calculate the heat of reaction at 90°C for the Sachse process (in which acetylene is made by partial combustion of LPG):



Thought Problems

1. When lava and water are mixed, an explosion can easily occur. Of course, the lava and water are not well mixed—only a short depth of the lava is contacted by the water. Nevertheless, what is the ratio of the mass of lava equivalent to the mass of an explosive that has a $\Delta H_{\text{rxn}}^\circ$ of about 4000 J/g? Data: C_p of lava is about 1 J/g and the temperature can be assumed to be 1100°C.
2. “Are fuel cells really green” is the heading of an article in a chemical engineering magazine. The article says that cells fueled with H_2 only omit water. Do fuel cells really represent a green technology?

Discussion Problems

1. Two men experimenting with a heating device in their garage noted that addition of water to their fuel always gave a hotter, brighter flame. Within no time, local press headlines blared: “Inventors Discover New Heater That Runs on Water!”

Although such sensational claims were obviously premature and unproved, the experimentation did lead to the development of a highly successful industrial burner, now marketed by Utah Hydro Corp. According to the Vice President of Utah Hydro, one of the two experimenters, a patent has just been granted on the device.

Known as the Hydro Oil Burner, the unit performs best on the cheapest of fuels—the higher the carbon content, the better. Jackson says that present users report savings from 33 to 50% of former oil consumption. And, combustion in the burner is so complete that soot, carbon, and smoke problems are nonexistent.

Dissociation may be key—hydro burners use steam as an atomizing agent. In operation, steam at 80–125 psi enters a superheating steam coil in the burner’s housing; the coil is fabricated of drawn stainless steel tubing. As the steam moves in a spiral path toward the discharge line leading to the burner nozzles, its temperature rises to about 1,000°F.

In theory, this high temperature, in combination with the low pressure within the combustion chamber, causes partial dissociation of the steam to hydrogen and oxygen. The hot gas–steam mixture then atomizes and thermally cracks the oil.

According to Utah Hydro, oxygen from the steam unites with carbon in the oil, and the released hydrogen is burned, thus apparently increasing the overall burner output.

- a. Do you believe this Hydro Oil burner will work at all?
 - b. Can this burner increase the amount of energy obtained from one pound of fuel oil?
 - c. Can this burner effect a savings of $\frac{1}{3}$ to $\frac{1}{2}$ in fuel oil consumption as claimed?
2. Eric Cottell, a British-born inventor, does not change base metals into gold, but he does mix oil and water—and these days that may be the most welcome alchemy of all. Cottell claims that in a furnace a blend of three parts oil and one part water burns so much more cleanly and efficiently than ordinary oil that it can cut fuel consumption by at least 20% while producing almost no soot or ash. He also claims that road tests show that a car can run on 18% water and 82% gasoline, and result in such a low output of pollutants that the engine does not need the mileage-robbing emission-control devices required on new cars.

Cottell says that when the emulsion prepared in his reactor is pumped into a furnace, the water droplets explode into superheated steam, shattering the oil droplets and exposing a maximum of the oil's surface. This provides quick, nearly complete burning.

What do you think about the claims?

25.3 Merging the Heat of Formation with the Sensible Heat of a Compound in Making an Energy Balance

In this section we explain how the heats of formation can be merged directly with the sensible heats and the phase changes, and thus bypass the direct calculation of the heat of reaction. The procedure is attractive from the viewpoint of using process simulators. The basic idea is to include $\Delta \hat{H}_f^\circ$ for each component in the enthalpy change for that component.

To illustrate the concept, consider the process illustrated in Figure 25.4, for which the reaction is



Assume that *nonstoichiometric amounts of reactants and products, respectively, enter and leave the reactor at different temperatures*. You cannot always assume that reactions occur with stoichiometric quantities of reactants, that the reactions go to completion, and that the temperatures of any of the inlet and outlet streams are the same. You should always **first choose a reference state** for the enthalpies at which the heats of formation are known, namely 25°C and 1 atm. (If no reaction takes place, the reference state can be the state of an inlet or outlet stream.)

The enthalpies of each stream entering and leaving **calculated relative to the selected reference state** will include three components for *every compound in the stream whether it is involved in the reaction or not*:

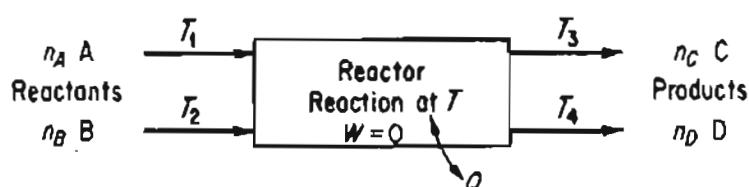


Figure 25.4 Steady-state flow process with reaction. The labels "Reactants" and "Products" can include compounds that may or may not react.

- (a) the standard heat of formation of the compound
- (b) the "sensible heat" of the compound (relative to the reference temperature)
- (c) any phase changes of the compound.

Because enthalpy is a state variable, you can choose any path you want to execute the calculations for the overall enthalpy change in a compound as long as you start and finish at the specified initial and final states, respectively. Figure 25.5 illustrates the idea. The reference state is chosen to be 25°C and 1 atm, the state at which the $\Delta \hat{H}_f^0$'s are known. In the figure, each component is treated separately, taking into account the respective number of moles and adding in any phase changes. (For our purposes here, we assume no enthalpy change occurs on mixing. Refer to Chapter 28 if heats of mixing are involved in the process.) In Figure 25.5, $T_C = T_D$. You could include pressure effects along with the illustrated temperature effects on the enthalpy, but we will omit in this book consideration of the effect of pressure except for problems in which the enthalpy data are easily retrieved from tables (such as the stream tables) or databases.

How do the enthalpy changes for each stream get introduced into the general energy balance?

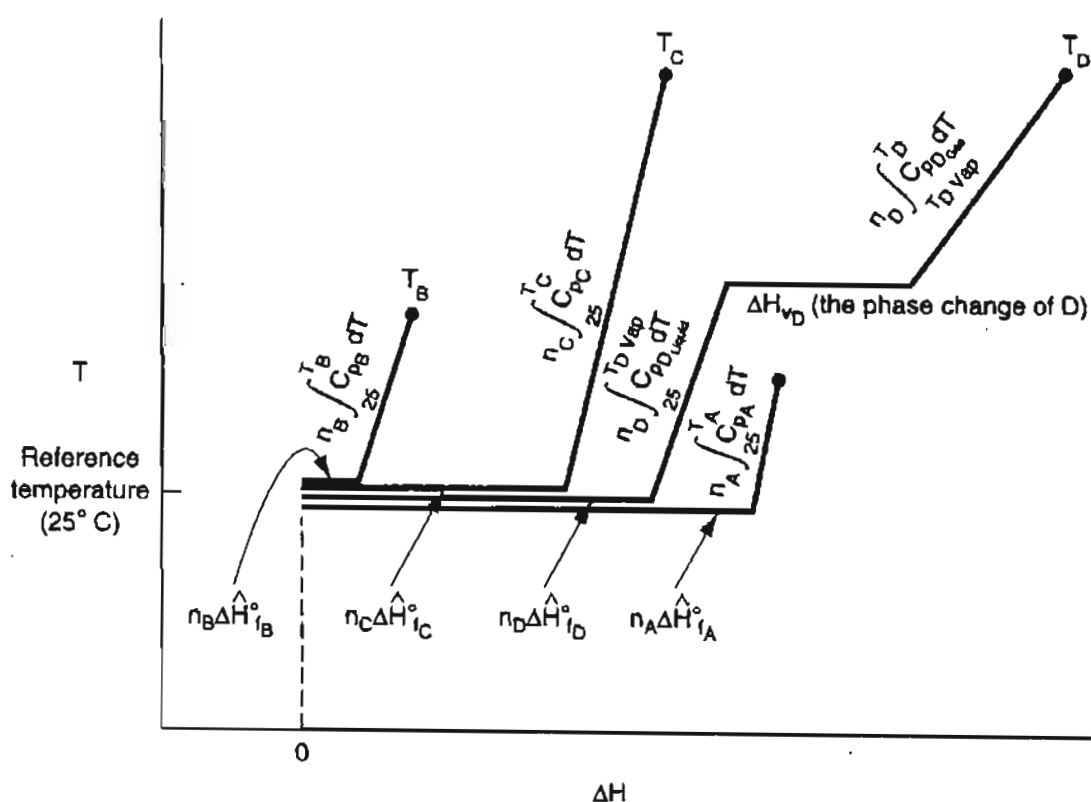


Figure 25.5 Illustration of how the enthalpy of each species entering and leaving the process shown in Figure 25.5 is calculated relative to the reference state of 25°C and 1 atm.

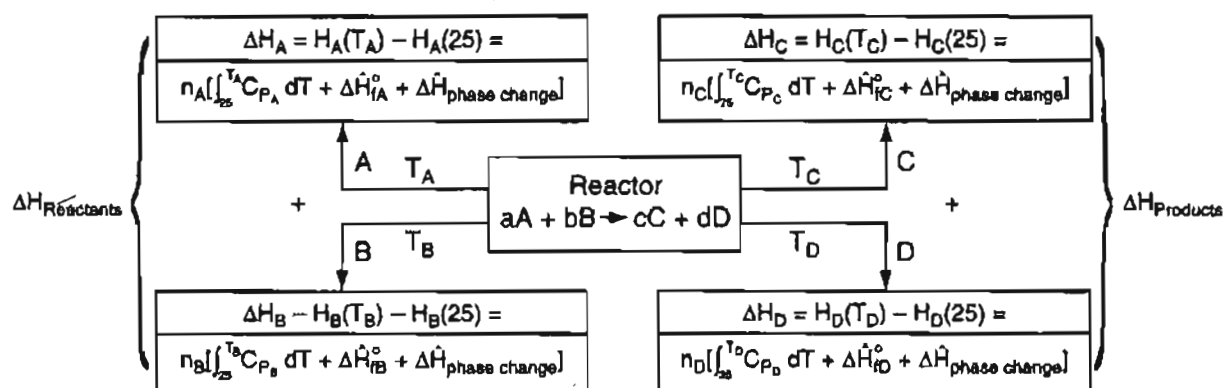


Figure 25.6 Information flow diagram showing how to calculate the enthalpies of the compounds entering and leaving a reactor.

To make the presentation simple, assume a steady-state flow process ($\Delta U = 0$) with no work ($W = 0$), and $KE = PE = 0$ so that the general energy balance reduces to

$$Q = \Delta H = \Delta H^{\text{out}} - \Delta H^{\text{in}} \quad (25.7)$$

Equation (25.7) includes all of the compounds entering and leaving whether they react or not. Rather than write a long equation, look at Figure 25.6, which shows how you calculate the values for the ΔH^{out} and ΔH^{in} .

Probably the easiest way to calculate ΔH^{out} and ΔH^{in} is to use enthalpy data for individual species obtained directly from published tables or databases such as on the CD in the back of this book. Do not forget to take into account phase changes, if they take place, in the enthalpy calculations if the phase enthalpy difference is not included in $\Delta \hat{H}_f^0$ or in the tables.

EXAMPLE 25.8 Example 25.4 Redone with the Heats of Formation Merged with the Sensible Heats

The problem and all of the data are in Example 25.4. The table below formulates the details of the solution.

Comp.	g mol	$T(^{\circ}\text{C})$	$\Delta \hat{H}_f^0 (\text{kJ/g mol})$	$\Delta \hat{H}_{25^{\circ}\text{C}}^{500^{\circ}\text{C}} (\text{kJ/g mol})$	$\Delta H (\text{kJ})$
<i>In</i>					
$\text{CO}_2(\text{g})$	1	500	-393.250	21.425	-371.825
$\text{H}_2(\text{g})$	4	500	0	13.834	55.336
				Total	-316.489
<i>Out</i>					
$\text{H}_2\text{O}(\text{g})$	2	500	-241.835	17.010	-449.650
$\text{CH}_4(\text{g})$	1	500	-74.848	23.126	-51.772
				Total	-501.442

Now, $Q = \Delta H = \Delta H^{\text{out}} - \Delta H^{\text{in}} = -501.442 - (-316.489) = -184.9 \text{ kJ}$

EXAMPLE 25.9 Calculation of the Heat Transfer When the Reactants and Products Enter and Leave at Different Temperatures

As an example of the application of Figure 25.6, let us calculate ΔH for the reaction shown in Figure E25.9.

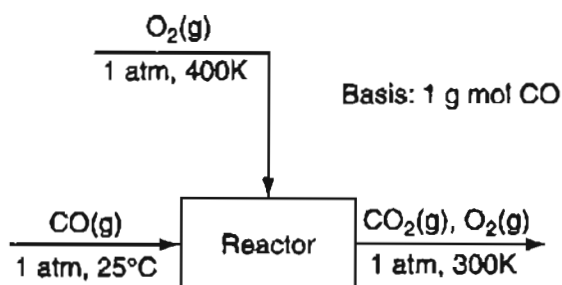
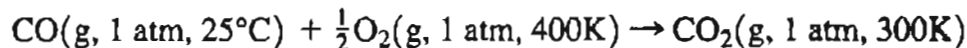


Figure E25.9

Assume nonstoichiometric quantities of compounds enter and leave with the moles and temperatures shown in columns 2 and 3 of the table below, respectively. The reaction equation is



Solution

Data you need to make the calculation (taken from Appendices D and E rather than integrating the heat capacity equations) are:

Compound	g mol	$T(^{\circ}\text{C})$	Heat of formation $\Delta \hat{H}_f^{\circ}$ (kJ/g mol)	Sensible heat $\Delta \hat{H}_{25^{\circ}\text{C}}^T$ (kJ/g mol)	Total ΔH (kJ)
<i>In</i>					
CO	1.0	25	-110.520	0	-110.520
O ₂	1.5	400	0	(12.351 - 0.732) = 11.619	17.429
<i>Out</i>					
CO ₂	1.0	300	-393.510	(12.556 - 0.912) = 11.644	-381.866
O ₂	1.0	300	0	(9.121 - 0.732) = 8.389	8.389

Note that in the tables in Appendix D, the reference temperature for $\hat{H} = 0$ is 0°C , not 25°C , so that the enthalpy at 25°C is subtracted in the sensible heat column for each compound.

Based on the above data

$$\Delta H = (-381.866 + 8.389) - (-110.520 + 17.429) = -280.386 \text{ kJ/g mol CO}$$

SELF-ASSESSMENT TEST

Questions

1. Explain why omitting the term for the heat of reaction at SC in the energy balance does not prevent you from obtaining the proper value of ΔH to use in the energy balance.
2. What are some of the advantages and disadvantages of calculating the enthalpy change of a compound in a process for use in an energy balance by the method described in Section 25.3 versus that in Section 25.2?

Problems

1. What is the heat transfer to or from a reactor in which methane reacts completely with oxygen to form carbon dioxide gas and water vapor? Base your calculations on a feed of 1 g mol of $\text{CH}_4(\text{g})$ at 400K plus 2 g mol of $\text{O}_2(\text{g})$ at 25°C. The exit gases leave at 1000K. Use the method of this section.
2. Repeat Problem #1, but assume that the fraction conversion is only 60%.
3. Calculate the heat added or removed from a reactor in which stoichiometric amounts of $\text{CO}(\text{g})$ and $\text{H}_2(\text{g})$ at 400°C react to form $\text{CH}_3\text{OH}(\text{g})$ (methanol) at 400°C.

Thought Problem

1. A review of additives to gasoline to give blends that improve its octane rating shows that oxygenated compounds necessarily contain lower energy (Btu per gallon). Dimethyl ether has a heat of reaction approximately equal to that of gasoline. Dimethyl ether costs 70 cents/gal, whereas unleaded premium gas costs 80 cents/gal (untaxed), so that the result may seem like a standoff.

Are the two fuels really equivalent in practical use?

Discussion Problems

1. An automobile owner sued his insurance company because his (lead-acid) battery exploded, damaging the hood and motor. The adjuster from the insurance company, after inspecting the remains of the battery, stated that his company was not liable to pay the claim because the battery grossly overheated.

Can a battery overheat? How? If overheating took place, why would the battery explode? What would be the most likely mechanism of the explosion?

2. As reported in the news, a tank car that normally carried ethylene oxide (EO) was turned over to a contractor for cleaning because off-color samples of EO were found during the off-loading of the tank car. At the start of the cleaning procedure the initial pressure in the car was 10 psig. A vent hose was connected to a caustic scrubber, and another hose was used to fill the tank with water that was stored for the firefighting system. After the operator filled the tank, he disconnected the vent line and noted an unexpected odor. Conse-

quently, the cleaning procedure was stopped and the tank car valves closed. Then the car was moved to a storage track.

In the middle of the night the tank car exploded, sending pieces of the car as far as 2500 feet away, damaging 10 other tank cars and several of the cleaning contractor's buildings. No one was injured.

On investigation, it was found that the Illinois Central Railroad had weighted the car in transit, and the weight indicated that the car had apparently contained 29,000 lb (1/6 of the volume) over the designated load weight that had been used in off-loading the EO in the car. Apparently this 29,000 lb was still in the tank car at the time cleaning was started (under the assumption that the tank was empty). Calculations showed that when filled with water, the EO, if mixed with the water, would lead to a 15% solution.

Investigators did not believe a 15% solution of EO in water could explode. The reaction is



Calculate the adiabatic reaction temperature rise for the tank car under the assumption that the EO was well mixed with the water.

Based on the results of these calculations, experiments were carried out on a similar tank car to see what happened in the cleaning process, and it was found that the EO did not mix much with the water. Instead the EO layer originally at the bottom of the tank rose to the top as the tank filled. A 50 cm layer of almost pure EO developed, under which a 25 cm layer of a mixture of EO and water occurred; and underneath lay a 200 cm layer of water.

Reactions of pure EO occur as follows:



Estimate the adiabatic reaction temperature of pure EO for each of these two reactions. Prepare a figure showing the estimated temperature in the tank as a function of the EO concentration (use 0, 20, 40, 60, 80, and 100%) on the axis.

Ignition of EO liquid was shown to take place above 450°C. What might a possible mechanism have been for the explosion? What recommendations would you make in preparing a tank car for cleaning?

25.4 The Heat of Combustion

An older method of calculating enthalpy changes when chemical reactions occur is via **standard heats (enthalpies) of combustion**, $\Delta \hat{H}_c^\circ$, which have a different set of reference conditions than do the standard heats of formation. The conventions used with the standard heats of combustion are:

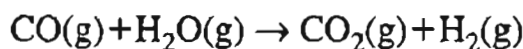
- The compound is oxidized with oxygen or some other substance to the products $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{HCl}(\text{aq})$, and so on.
- The reference conditions are still 25°C and 1 atm.
- Zero values of $\Delta\hat{H}_c^\circ$ are assigned to certain of the oxidation products as, for example, $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{HCl}(\text{aq})$, and to $\text{O}_2(\text{g})$ itself.
- If other oxidizing substances are present, such as S or N_2 or if Cl_2 is present, it is necessary to *make sure that states of the products are carefully specified and are identical to (or can be transformed into) conditions that determine the standard state.*
- Stoichiometric quantities are assumed to react completely.

The heat of combustion has been proposed as one of the criteria to determine the ranking of the incinerability of hazardous waste. The rationale is that if a compound has a higher heat of combustion it can release more energy than other compounds during combustion, and would be easier to incinerate. You can calculate a standard heat of reaction using the heats of combustion by an equation analogous to Equation (25.1).

$$\Delta H_{\text{rxn}}^\circ(25^\circ\text{C}) = - \left(\sum_{\text{Products}} n_i \Delta\hat{H}_{c,i}^\circ - \sum_{\text{Reactants}} n_i \Delta\hat{H}_{c,i}^\circ \right) \quad (25.7)$$

Note: The minus sign in front of the summation expression occurs because the choice of reference states is zero for the righthand products of the standard reaction. Refer to Appendix F for values of $\Delta\hat{H}_c^\circ$.

As an example of the calculation of $\Delta H_{\text{rxn}}^\circ(25^\circ\text{C})$ from heat of combustion data, we will calculate $\Delta H_{\text{rxn}}^\circ(25^\circ\text{C})$ for the reaction (the data are taken from Appendix F in kJ/g mol).



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ(25^\circ\text{C}) &= - \{ [(1)(0) + (1)(-285.84)] - [(1)(-282.99) + (1)(-44.00)] \} \\ &= -41.15 \text{ kJ} \end{aligned}$$

Note that the heat of combustion of $\text{H}_2\text{O}(\text{l})$ is zero, but is -44.00 kJ/g mol for $\text{H}_2\text{O}(\text{g})$ —you have to subtract the heat of vaporization of water at 25°C and 1 atm from the value for $\text{H}_2\text{O}(\text{l})$. (Look at Figure 25.9 as to the source of the $\Delta\hat{H}_{\text{vap}} = 44.00$ kJ/g mol.)

For a fuel such as coal or oil, the *negative* of the standard heat of combustion is known as the **heating value** of the fuel. Both a **lower (net) heating value (LHV)** and a **higher (gross) heating value (HHV)** exist, depending upon whether the water in the combustion products is in the form of a vapor (for the LHV) or a liquid (for the HHV). For H_2O

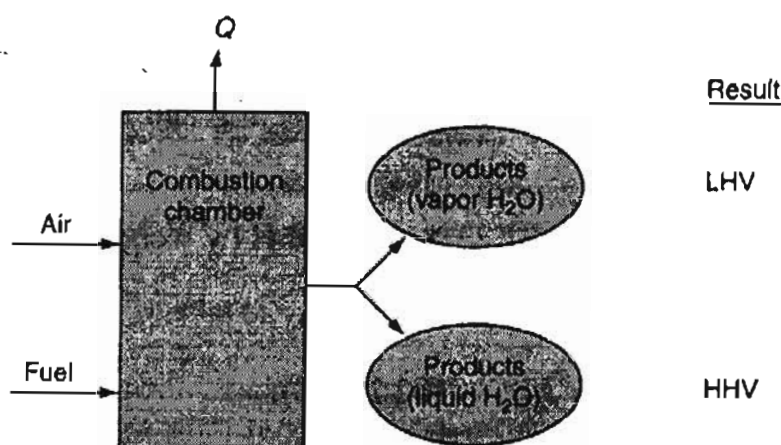


Figure 25.7 The classification of LHV or HHV for a fuel depends on the state of the water exiting from the system.

$$\text{HHV} = \text{LHV} + (n_{\text{H}_2\text{O}(\text{g}) \text{ in product}} \times \Delta \hat{H}_{\text{vap}} \text{ at } 25^\circ\text{C and } 1 \text{ atm}).$$

Look at Figure 25.7.

The precise heat of vaporization for a compound such as water at 1 atm and 25°C can be calculated as shown in Figure 25.8, but the value of heat of vaporization of a compound at 25°C and the vapor pressure of the compound will suffice for engineering calculations.

Calculation of the heat of reaction for fuels and compounds with complicated analysis requires you to use empirical formulas to estimate $\Delta \hat{H}_{\text{rxn}}^\circ$. You can estimate the heating value of a coal within about 3% from the Dulong formula*:

Higher heating value (HHV) in Btu per pound

$$= 14,544 C + 62,028 \left(H - \frac{O}{8} \right) + 4050 S$$

$$\Delta \hat{H}_{\text{vap}}^\circ \text{ at } 25^\circ\text{C and } 1 \text{ atm} = 44.000 \text{ J/g mol} \left\{ \begin{array}{l} \text{H}_2\text{O}(\text{l}) \text{ } 25^\circ\text{C, } 1 \text{ atm} \\ \downarrow \Delta H_1 \cong 0 \text{ J/g mol} \\ \text{H}_2\text{O}(\text{l}) \text{ } 25^\circ\text{C, vapor pressure at } 25^\circ\text{C} \\ \downarrow \Delta H_2 = \Delta H_{\text{vap}} \text{ at the vapor pressure of water} \\ \quad (p = 3.17 \text{ kPa}) = 44,004 \text{ J/g mol} \\ \text{H}_2\text{O}(\text{g}) \text{ } 25^\circ\text{C, vapor pressure at } 25^\circ\text{C} \\ \downarrow \Delta H_3 = -4 \text{ J/g mol} \\ \text{H}_2\text{O}(\text{g}) \text{ } 25^\circ\text{C, } 1 \text{ atm} \end{array} \right.$$

Figure 25.8 The enthalpy change that occurs when H₂O(l) goes from 25°C and 1 atm to H₂O(g) at 25°C and 1 atm.

*H. H. Lowry, ed. *Chemistry of Coal Utilization*, Wiley, New York, (1945), Chap. 4.

where C is the weight fraction carbon, H is the weight fraction hydrogen, and S is the weight fraction sulfur. The values of C , H , S , and O can be taken from the fuel or the flue-gas analysis. A general relation between the gross heating and net heating values is

$$\text{net Btu/lb coal} = \text{gross Btu/lb coal} - 91.23 \times (\% \text{ total H by weight})$$

The HHV of fuel oils in Btu per pound can be approximated by

$$\text{HHV} = 17,887 + 57.5^\circ\text{API} - 102.2 (\%S).$$

There's no fuel like an old fuel.

Anonymous

EXAMPLE 25.10 Heating Value of Coal

Coal gasification consists of the chemical transformation of solid coal into a combustible gas. For many years before the widespread adoption of natural gas, gas generated from coal served as a fuel (and also as an illuminant). The heating values of coals differ, but the higher the heating value, the higher the value of the gas produced. The analysis of the following coal has a reported heating value of 29,770 kJ/kg as received. Assume that this is the gross heating value at 1 atm and 25°C obtained in an open system.** Use the Dulong formula to check the validity of the reported value.

Component	Percent
C	71.0
H ₂	5.6
N ₂	1.6
Net S	2.7
Ash	6.1
O ₂	13.0
Total	100.0

Solution

$$\begin{aligned} \text{HHV} &= 14,544(0.71) + 62,028 \left[(0.056) - \frac{0.130}{8} \right] + 4050(0.027) \\ &= 12,901 \text{ Btu/lb} \end{aligned}$$

Note 0.056 lb of H₂ is also 0.056 lb of H, and 0.130 lb of O₂ is 0.130 lb of O.

**If the reported value was obtained in a closed system as might be the case, the value reported might be $\Delta\hat{U}$, not $\Delta\hat{H}$, hence $\Delta\hat{H}$ would have to be calculated from $\Delta\hat{U} + \Delta(p\hat{V})$ for the experiment.

$$\frac{12,901 \text{ Btu}}{\text{lb}} \left| \frac{1 \text{ lb}}{0.454 \text{ kg}} \right| \frac{1.055 \text{ kJ}}{1 \text{ Btu}} = 29,980 \text{ kJ/kg}$$

The two values are quite close.

EXAMPLE 25.11 Selecting a Fuel to Reduce SO₂ Emissions

SO₂ emissions from power plants are the primary source of acid rain, that is, SO₂ in the atmosphere is absorbed by rain, thus increasing the acidity of lakes and rivers. Consider the two fuels listed in the table below. Determine which fuel would be preferred to provide 10⁶ Btu of thermal energy from combustion while minimizing the SO₂ emissions. SO₂ removal from the flue gas can be implemented to reduce the SO₂ discharge, but at additional cost, bringing into play another important factor in choosing a fuel.

	No. 6 Fuel Oil	No. 2 Fuel Oil
Density (lb/ft ³)	60.2	58.7
Lower heating value (Btu/gal)	155,000	120,000
Carbon (wt %)	87.2	87.3
Hydrogen (wt %)	10.5	12.6
Sulfur (wt %)	0.72	0.62
Ash (wt %)	0.04	<0.01

Solution

Basis: 10⁶ Btu from combustion

For No. 6 Heating Oil:

$$\frac{10^6 \text{ Btu}}{155,000 \text{ Btu}} \left| \frac{1 \text{ gal}}{60.2 \text{ lb fuel}} \right| \frac{0.0072 \text{ lb S}}{1 \text{ lb fuel}} = 2.80 \text{ lb S}$$

For No. 2 Heating Oil:

$$\frac{10^6 \text{ Btu}}{120,000 \text{ Btu}} \left| \frac{1 \text{ gal}}{58.7 \text{ lb fuel}} \right| \frac{0.0062 \text{ lb S}}{1 \text{ lb fuel}} = 3.03 \text{ lb S}$$

The No. 6 Heating Oil should be selected because its combustion will generate less SO₂ emissions, even though it has a higher weight percent S.

SELF-ASSESSMENT TEST

Questions

1. Explain why in calculating ΔH using heats of formation you subtract ΔH of the inputs from the ΔH of the outputs, whereas in using heat of combustion you subtract the ΔH of the outputs from that of the inputs.
2. Can the HHV ever be the same as the LHV?
3. Can the HHV ever be lower than the LHV?
4. Do you have to use heats of combustion to calculate a HHV or a LHV?
5. Is it true for the reaction $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ at 25°C and 1 atm, which has a cited heat of reaction of -241.83 kJ , that if you write the reaction as $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$, the calculated heat of reaction will be $2(-241.83) \text{ kJ}$?
6. What is the difference in HHV and LHV when CO is burned with O_2 at 25°C and 1 atm?

Problems

1. A synthetic gas analyzes 6.1% CO_2 , 0.8% C_2H_4 , 0.1% O_2 , 26.4% CO, 30.2% H_2 , 3.8% CH_4 , and 32.6% N_2 . What is the heating value of the gas measured at 60°F , saturated when the barometer reads 30.0 in Hg?
2. Calculate the standard heat of reaction using heat of combustion data for the reaction
$$\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l})$$
3. Start with the Dulong equation, and give an equation for the LHV in terms of HHV and the variables in the Dulong equation and the percent water (W) in the fuel.

Thought Problems

1. Thermal destruction systems have become recognized over the past decade as an increasingly desirable alternative to the more traditional methods of disposing of hazardous wastes in landfills and injection wells. What are some of the problems in the combustion of substances such as methylene chloride, chloroform, trichloroethylene, waste oil, phenol, aniline, and hexachloroethane?
2. How does the presence of a diluent or excess reactant alter the heat effects associated with an exothermic reaction?
3. What is the effect of nonstoichiometric quantities of reactants on the standard heat of reaction?
4. In gas turbine cogeneration and combined cycle projects the heat recovery stream generator may be fired with auxiliary fuel in order to generate additional steam. One of the frequently asked questions concerns the consumption of oxygen in the exhaust gas versus fuel quantity fired. Would there be sufficient oxygen in the exhaust to raise the exhaust gas to the desired temperature?

Discussion Problem

1. As an interest in synthetic fuel projects develops, allegations about the health and environmental risks associated with these projects increase. From process descriptions it is not

always clear why certain projects gain rapid acceptance whereas others do not. For example, coal gasification and liquefaction processes are cited as contributing to a "greenhouse effect" by releasing more CO_2 to the atmosphere than oil or natural gas. On the other hand, the use of alcohol as a fuel is considered to be an acceptable CO_2 release.

A recent issue of *Energy Resources & Technology* describes plans for a 60,000 bbl per day ethanol plant for fuel production. The plant will consume 86,600 Btu of energy to produce 1 gal of ethyl alcohol, plus a cattle feed by-product having "an energy equivalent of 14,500 Btu." Since combustion of 1 gal of alcohol yields 76,500 Btu, the total energy produced on burning the alcohol is 4400 Btu greater than that consumed in its production.

Calculations show that this overall process yields 7500 Btu of energy per mole of CO_2 produced. Efficient coal conversion processes produce 140,000 Btu for each mole of CO_2 produced. This is almost 19 times the energy produced from alcohol at equivalent CO_2 production.

Is fuel production from alcohol attractive?

Looking Back

In this chapter we explained three ways of adjusting the value of ΔH in the energy balance to take into account reactions that occur in the system by using (1) heats of reaction, (2) heats of formation, and (3) heats of combustion. All three techniques will give equivalent results.

GLOSSARY OF NEW WORDS

Endothermic reaction The reverse of an exothermic reaction.

Exothermic reaction The energy required to hold the products of the reaction together is less than that required to hold the reactants together, and the internal energy of a system will increase, heat will be transferred, or both occur.

Heat of reaction Enthalpy change that is associated with a reaction.

Heating value The negative of the standard heat of combustion for a fuel such as coal or oil.

Higher (gross) heating value (HHV) Value of negative heat of combustion when the product water is a liquid.

Lower (net) heating value (LHV) Value of the negative of the heat of combustion when the product water is a vapor.

Reference state For enthalpy it is the state at which the enthalpy is zero.

Sensible heat The quantity $(\hat{H}_{T,p} - \hat{H}_{\text{ref}}^0)$, which excludes any phase changes.

Standard heat of combustion Enthalpy change for the oxidation of 1 mole of a compound at 25°C and 1 atm. By definition the water and carbon dioxide on the righthand side of the reaction equation are assigned zero values.

Standard heat of formation Enthalpy change for the formation of 1 mole of a compound from its constituent elements at 25°C and 1 atm.

Standard heat of reaction Heat of reaction for components in the standard state (25°C and 1 atm) when stoichiometric quantities of reactants react completely to give products at 25°C and 1 atm.

Standard state For the heat of reaction, 25°C and 1 atm.

SUPPLEMENTARY REFERENCES

In addition to the general references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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Web Sites

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<http://webbook.nist.gov/>

<http://www.aiche.org/dippr/projects/871.htm>

<http://www.asu.edu/lib/noble/chem/prop-gh.htm>

<http://www.cachesoftware.com/mopac/Mopac2002manual/node510.html>

<http://www.owl.net.rice.edu/~ceng301/34.html>

PROBLEMS

- *25.1** Which of the following heats of formation would indicate an endothermic reaction? (1) -32.5 kJ; (2) 32.5 kJ (3) -82 kJ; (4) 82 kJ; (5) both (1) and (3); (6) both (2) and (4).
- *25.2** Which of the following changes of phase is exothermic? (1) gas to liquid; (2) solid to liquid; (3) solid to gas; (4) liquid to gas.
- *25.3** Exothermic reactions are usually self-sustaining because (1) exothermic reactions usually require low activation energies; (2) exothermic reactions usually require high activation energies; (3) the energy released is sufficient to maintain the reaction; (4) the products contain more potential energy than the reactants.
- **25.4** The following enthalpy changes are known for reactions at 25°C and one atm.

No.			ΔH° (kJ/gmol)
1	$\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g})$	$\longrightarrow \text{C}_3\text{H}_8(\text{g})$	-123.8
2	$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g})$	$\longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	-2220.0
3	$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	$\longrightarrow \text{H}_2\text{O}(\text{l})$	-285.8
4	$\text{H}_2\text{O}(\text{l})$	$\longrightarrow \text{H}_2\text{O}(\text{g})$	43.9
5	$\text{C}(\text{diamond}) + \text{O}_2(\text{g})$	$\longrightarrow \text{CO}_2(\text{g})$	-395.4
6	$\text{C}(\text{graphite}) + \text{O}_2(\text{g})$	$\longrightarrow \text{CO}_2(\text{g})$	-393.5

Calculate the heat of formation of propylene (C_3H_6).

- *25.5** How would you determine the heat of formation of gaseous fluorine at 25°C and 1 atm?
- **25.6** In a fluidized bed gasification system you are asked to find out the heat of formation of a solid sludge of the composition (formula) C_5H_2 from the following data:

		ΔH (kJ/gmol)
$\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$	$\longrightarrow \text{CO}(\text{g})$	-110.4 kJ/gmol C
$\text{C}(\text{s}) + \text{O}_2(\text{g})$	$\longrightarrow \text{CO}_2(\text{g})$	-394.1 kJ/gmol C
$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	$\longrightarrow \text{H}_2\text{O}(\text{g})$	-241.826 kJ/gmol H_2
$\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	$\longrightarrow \text{CO}_2(\text{g})$	-283.7 kJ/gmol CO
$\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$	$\longrightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$	-38.4 kJ/gmol H_2O
$\text{C}_5\text{H}_2(\text{s}) + 5\frac{1}{2}\text{O}_2(\text{g})$	$\longrightarrow 5\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	-2110.5 kJ/gmol C_5H_2
ΔH vaporization H_2O at 25°C		$+43.911$ kJ/gmol H_2O_2

*25.7 Look up the heat of formation of

- (a) liquid ammonia
- (b) formaldehyde gas
- (c) acetaldehyde liquid

If you can't find the value, get data to calculate it.

**25.8 J. D. Park et al. [JACS 72, 331-3 (1950)] determined the heat of hydrobromination of propene (propylene) and cyclopropane. For hydrobromination (addition of HBr) of propene to 2-bromopropane, they found that $\Delta H = -84,441$ J/g mol. The heat of hydrogenation of propene to propane is $\Delta H = -126,000$ J/g mol. N.B.S. Circ. 500 gives the heat of formation of HBr(g) as $-36,233$ J/g mol when the bromine is liquid, and the heat of vaporization of bromine as $30,710$ J/g mol. Calculate the heat of bromination of propane using gaseous bromine to form 2-bromopropane using the above data.

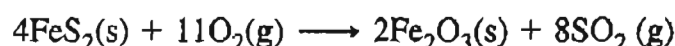
*25.9 Calculate the standard (25°C and 1 atm) heat of reaction per g mol of the first reactant on the left-hand side of the reaction equation for the following reactions:

- (a) $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$
- (b) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
- (c) $\text{C}_6\text{H}_{12}(\text{g}) \longrightarrow \text{C}_6\text{H}_6(\text{l}) + 3\text{H}_2(\text{g})$
cyclohexane benzene

*25.10 Calculate the standard heat of reaction for the following reactions:

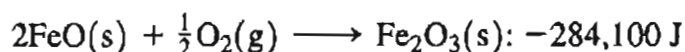
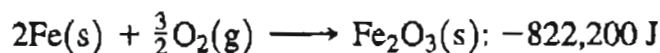
- (a) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
- (b) $2\text{CaO}(\text{s}) + 2\text{MgO}(\text{s}) + 4\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Ca}(\text{OH})_2(\text{s}) + 2\text{Mg}(\text{OH})_2(\text{s})$
- (c) $\text{Na}_2\text{SO}_4(\text{s}) + \text{C}(\text{s}) \longrightarrow \text{Na}_2\text{SO}_3(\text{s}) + \text{CO}(\text{g})$
- (d) $\text{NaCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \longrightarrow \text{NaHSO}_4(\text{s}) + \text{HCl}(\text{g})$
- (e) $\text{NaCl}(\text{s}) + 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \longrightarrow 2\text{Na}_2\text{SO}_4(\text{s}) + 4\text{HCl}(\text{g})$
- (f) $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{SO}_4(\text{l})$
- (g) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
- (h) $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{Na}_2\text{S}(\text{s}) + 4\text{SO}_2(\text{g}) \longrightarrow 3\text{Na}_2\text{S}_2\text{O}_3(\text{s}) + \text{CO}_2(\text{g})$
- (i) $\text{CS}_2(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow \text{S}_2\text{Cl}_2(\text{l}) + \text{CCl}_4(\text{l})$
- (j) $\text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{CH}_3\text{CH}_2\text{Cl}(\text{g})$
ethylene ethylchloride
- (k) $\text{CH}_3\text{OH}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$
methyl alcohol formaldehyde
- (l) $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_3\text{CHO}(\text{l})$
acetylene acetaldehyde
- (m) $n\text{-C}_4\text{H}_{10}(\text{g}) \longrightarrow \text{C}_2\text{H}_4(\text{g}) + \text{C}_2\text{H}_6(\text{g})$
butane ethylene ethane

*25.11 In the reaction

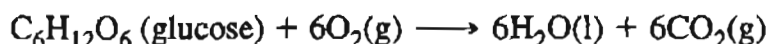


the conversion of $\text{FeS}_2(\text{s})$ to $\text{Fe}_2\text{O}_3(\text{s})$ is only 80% complete. If the standard heat of reaction for the reaction is calculated to be -567.4 kJ/g mol $\text{FeS}_2(\text{s})$, what value of $\Delta H_{\text{rxn}}^\circ$ will you use per kg of FeS_2 burned in an energy balance?

- *25.12** Determine the standard heat of formation for FeO(s) given the following values for the heats of reaction at 25°C and 1 atm for the following reactions:



- **25.13** Physicians measure the metabolic rate of conversion of foodstuffs in the body by using tables that list the liters of O_2 consumed per gram of foodstuff. For a simple case, suppose that glucose reacts

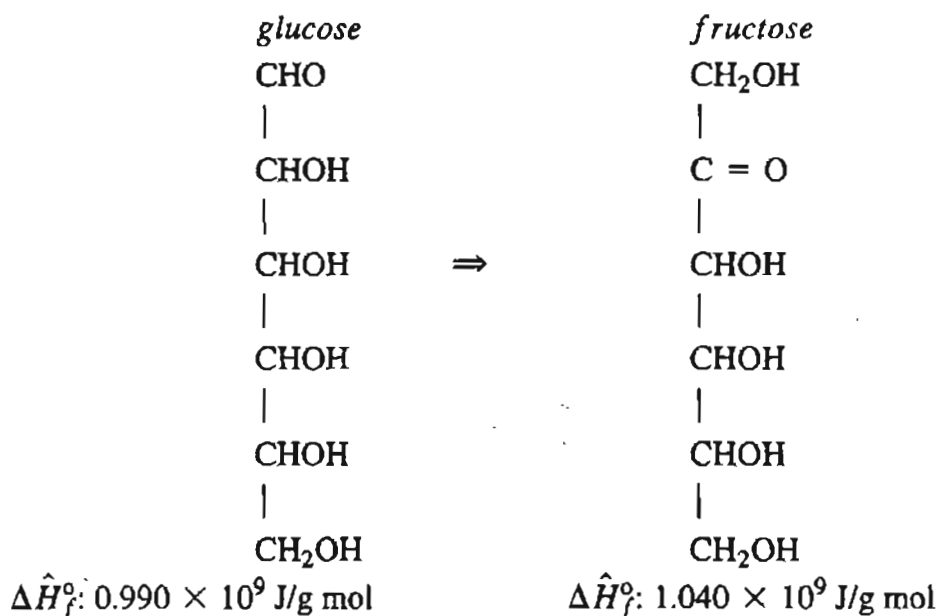


How many liters of O_2 would be measured for the reaction of one gram of glucose (alone) if the conversion were 90% complete in your body? How many kJ/g of glucose would be produced in the body? *Data:* $\Delta \hat{H}_f^\circ$ of glucose is -1260 kJ/g mol of glucose. Ignore the fact that your body is at 37°C , and assume it is at 25°C .

- *25.14** M. Beck et al. (*Can J. Ch.E.*, 64 (1986): 553) described the use of immobilized enzymes (E) in a bioreactor to convert glucose (G) to fructose (F).

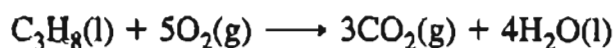


At equilibrium the overall reaction can be considered to be $\text{G} + \text{E} \longleftrightarrow \text{E} + \text{F}$.



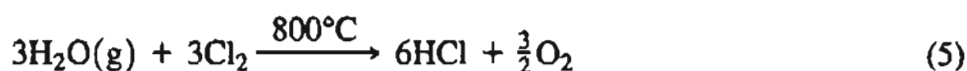
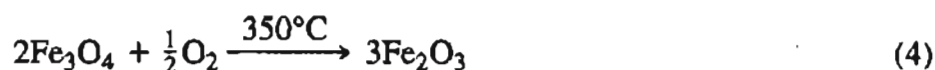
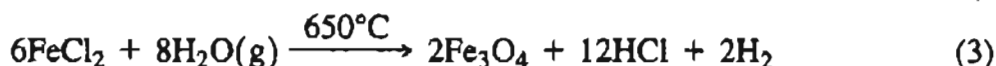
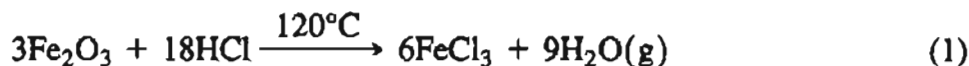
The fraction conversion is a function of the flow rate through the reactor and the size of the reactor, but for a flow rate of $3 \times 10^{-3} \text{ m/s}$ and a bed height of 0.44 m, the fraction conversion on a pass through the reactor was 0.48. Calculate the heat of reaction at 25°C per mole of G converted.

- **25.15** Calculate the heat of reaction in the standard state for 1 mole of $\text{C}_3\text{H}_8(\text{l})$ for the following reaction from the given data:



Compound	$-\Delta\hat{H}_f^\circ$ (kcal/g mol)	Vaporization at 25°C (kcal/g mol)
$\text{C}_3\text{H}_8(\text{g})$	24.820	3.823
$\text{CO}_2(\text{g})$	94.052	1.263
$\text{H}_2\text{O}(\text{g})$	57.798	10.519

****25.16** Hydrogen is used in many industrial processes, such as the production of ammonia for fertilizer. Hydrogen also has been considered to have a potential as an energy source because its combustion yields a clean product and it is easily stored in the form of a metal hydride. Thermochemical cycles (a series of reactions resulting in a recycle of some of the reactants) can be used in the production of hydrogen from an abundant natural compound—water. One process involving a series of five steps is outlined in P25.16. State assumptions about the states of the compounds.



(a) Calculate the standard heat of reaction for each step.

(b) What is the overall reaction? What is its standard heat of reaction?

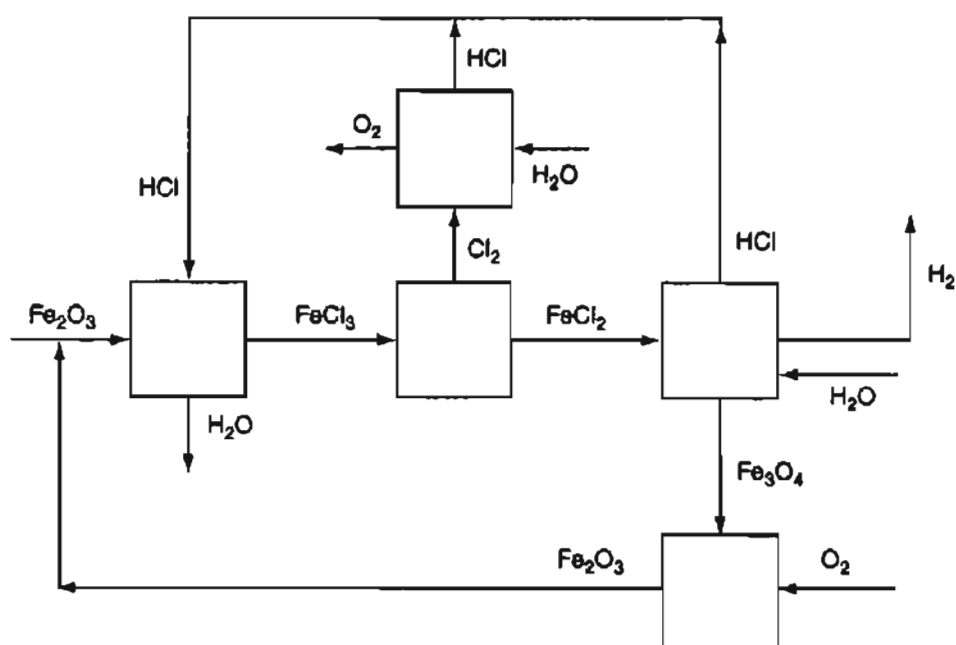
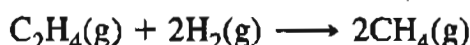


Figure P25.16

- **25.17** About 30% of crude oil is processed eventually into automobile gasoline. As petroleum prices rise and resources dwindle, alternatives must be found. However, automobile engines can be tuned so that they will run on simple alcohols. Methanol and ethanol can be derived from coal or plant biomass, respectively. While the alcohols produce fewer pollutants than gasoline, they also reduce the travel radius of a tank of fuel. What percent increase in the size of fuel tank is needed to give an equivalent travel radius if gasoline is replaced by alcohol? Base your calculations on 40 kJ/g of gasoline having a sp gr of 0.84, and with the product water as a gas. Make the calculations for (a) methanol; (b) ethanol.
- **25.18** A consulting laboratory is called upon to determine the heat of reaction at 25°C of a natural gas in which the combustible is entirely methane. They do not have a Sargent flow calorimeter, but do have a Parr bomb calorimeter. They pump a measured volume of the natural gas into the Parr bomb, add oxygen to give a total pressure of 1000 kPa, and explode the gas-O₂ mixture with a hot wire. From the data they calculate that the gas has a heating value of 39.97 kJ/m³. Should they report this value as the heat of reaction? Explain. What value should they report?
- **25.19** Calculate the heat transfer for the following reaction if it takes place at constant volume and a constant temperature of 25°C.



- **25.20** If 1 lb mol of Cu and 1 lb mol of H₂SO₄ (100%) react together completely in a bomb calorimeter, how many Btu are absorbed (or evolved)? Assume that the products are H₂(g) and CuSO₄. The initial and final temperatures in the bomb are 25°C.
- *25.21** Is it possible to calculate the heat of reaction by using property tables that are prepared using different reference states? How?
- *25.22** A fat is a glycerol molecule bonded to a combination of fatty acids or hydrocarbon chains. Usually, the glycerol bonds to three fatty acids, forming a triglyceride. A fat that has no double bonds between the carbon atoms in the fatty acid is said to be saturated.

How are fats treated by the human digestive system? They are first enzymatically broken down into smaller units, fatty acids and glycerol. This is called digestion and occurs in the intestine or cellularly by lysosomes. Next, enzymes remove two carbons at a time from the carboxyl end of the chain, a process which produces molecules of acetyl CoA, NADH and FADH₂. The acetyl CoA is a high energy molecule that is then treated by the Citric Acid Cycle which oxidizes it to CO₂ and H₂O.

Calculate the heat of reaction when tristearin is used in the body.

Data:	$\Delta \hat{H}_f^\circ$ (kJ/gmol)
Stearic acid (s) (C ₁₈ H ₃₆ O ₂), a fatty acid	-964.3
Glycerol(l) (C ₃ H ₈ O ₃)	-159.16
Tristearin(s) (C ₆₃ H ₁₃₂ O ₁₅), a triglyceride	-3.820

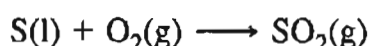
- *25.23** Answer the following questions briefly (no more than 3 sentences);
- Does the addition of an inert diluent to the reactants entering an exothermic process increase, decrease, or make no change in the heat transfer to or from the process?

- b. If the reaction in a process is incomplete, what is the effect on the value of the standard heat of reaction? Does it go up, down, or remain the same?
- c. Consider the reaction $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$. Is the heat of reaction with the reactants entering and the products leaving at 500K higher, lower, or the same as the standard heat of reaction?

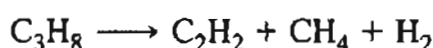
***25.24** Does the enthalpy of formation of a substance change with temperature?

***25.25** The $\Delta \hat{H}_f^\circ$ of N_2 is listed as zero. Does this mean that N_2 contains no energy at the standard reference state?

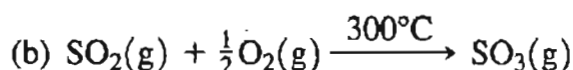
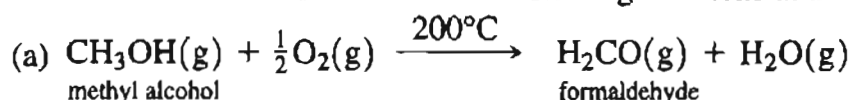
****25.26** Compute the heat of reaction at 600 K for the following reaction:



****25.27** Calculate the heat of reaction at 500°C for the decomposition of propane.



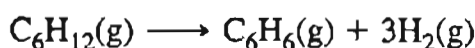
****25.28** Calculate the heat of reaction of the following reactions at the stated temperature:



****25.29** In a new process for the recovery of tin from low-grade ores, it is desired to oxidize stannous oxide, SnO , to stannic oxide, SnO_2 , which is then soluble in a caustic solution. What is the heat of reaction at 90°C and 1 atm for the reaction $\text{SnO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{SnO}_2$? Data are:

	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	C_p [J/(g mol)(K)], T in K
SnO	-283.3	$39.33 + 15.15 \times 10^{-3} T$
SnO ₂	-577.8	$73.89 + 10.04 \times 10^{-3} T - \frac{2.16 \times 10^4}{T^2}$

****25.30** Calculate the standard heat of reaction for the conversion of cyclohexane to benzene



If the reactor for the conversion operates at 70% conversion of C_6H_{12} , what is the heat removed from or added to the reactor if

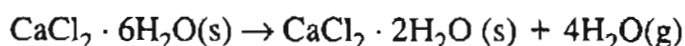
(a) the exit gases leave at 25°C?

(b) the exit gases leave at 300°C?

and the entering materials consist of C_6H_{12} together with one-half mole of N_2 per mole of C_6H_{12} , both at 25°C.

***25.31** One hundred gram moles of CO at 300°C is burned with 100 gram moles of O_2 which is at 100°C; the exit gases leave at 400°C. What is the heat transfer to or from the system in kJ?

- ***25.32** Calculate the pounds of carbon dioxide emitted per gallon of fuel for three fuels: (a) ethanol (C_2H_5OH), (b) benzene (C_6H_6), and (c) isooctane (C_8H_{18}), i.e., 2,2,4-trimethyl pentane. Compare the lb CO_2 /Btu and the Btu per gal of fuel for the respective reactions with the stoichiometric quantity of air entering the process at $100^\circ C$ and the other compounds entering and leaving at $77^\circ F$.
- **25.33** A synthesis gas at $500^\circ C$ that analyzes 6.4% CO_2 , 0.2% O_2 , 40.0% CO , 50.8% H_2 , and the balance N_2 is burned with 40% dry excess air which is at $25^\circ C$. The composition of the flue gas which is at $720^\circ C$ is 13.0% CO_2 , 14.3% H_2O , 67.6% N_2 and 5.1% O_2 . What was the heat transfer to or from the combustion process?
- **25.34** Dry coke composed of 4% inert solids (ash), 90% carbon, and 6% hydrogen at $40^\circ C$ is burned in a furnace with dry air at $40^\circ C$. The solid refuse at $200^\circ C$ that leaves the furnace contains 10% carbon and 90% inert, and no hydrogen. The ash does not react. The Orsat analysis of the flue gas which is at $1100^\circ C$ gives 13.9% CO_2 , 0.8% CO , 4.3% O_2 , and 81.0% N_2 . Calculate the heat transfer to or from the process. Use a constant C_p for the inert of 8.5 J/g.
- ***25.35** An eight room house requires 200,000 Btu per day to maintain the interior at $68^\circ F$. How much calcium chloride hexahydrate must be used to store the energy collected by a solar collector for one day of heating? The storage process involves heating the $CaCl_2 \cdot 6H_2O$ from $68^\circ F$ to $86^\circ F$, and then converting the hexahydrate to dihydrate and gaseous water:



The water from the dehydration is evaporated during the process. Use the following data:

	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	C_p (J/(g)($^\circ C$))
$CaCl_2 \cdot 6H_2O(s)$	-2607.89	1.34
$CaCl_2 \cdot 2H_2O(s)$	-1402.90	0.97

- **25.36** Calculate the heat of reaction at SC for 1 g mol of $H_2(g)$ using the heat of combustion data, and then calculate ΔH_{rxn} for $H_2(g)$ at $0^\circ C$.
- *25.37** Estimate the higher heating value (HHV) and lower heating value (LHV) of the following fuels in Btu/lb:
- (a) Coal with the analysis C (80%), H (0.3%), O (0.5%), S (0.6%), and ash (18.60%).
- (b) Fuel oil that is 30°API and contains 12.05% H and 0.5% S.
- *25.38** Is the higher heating value of a fuel ever equal to the lower heating value? Explain.
- *25.39** Find the higher (gross) heating value of $H_2(g)$ at $0^\circ C$.
- *25.40** The chemist for a gas company finds a gas analyzes 9.2% CO_2 , 0.4% C_2H_4 , 20.9% CO , 15.6% H_2 , 1.9% CH_4 , and 52.0% N_2 . What should the chemist report as the gross heating value of the gas?
- **25.41** What is the higher heating value of 1 m³ of *n*-propylbenzene measured at $25^\circ C$ and 1 atm and with a relative humidity of 40%?

- **25.42** An off-gas from a crude oil topping plant has the following composition:

Component	Vol. %
Methane	88
Ethane	6
Propane	4
Butane	2

(a) Calculate the higher heating value on the following bases: (1) Btu per pound, (2) Btu per lb mole, and (3) Btu per cubic foot of off-gas measured at 60°F and 760 mm Hg.

(b) Calculate the lower heating value on the same three bases indicated in part (a).

- *25.43** The label on a 43 gram High Energy ("Start the day with High Energy") bar states that the bar contains 10 grams of fat, 28 grams of carbohydrate, and 4 grams of protein. The label also says that the bar has 200 calories per serving (the serving size is 1 bar). Does this information agree with the information about the contents of the bar?

Data:

Component	$\Delta \hat{H}_c^\circ$ (kJ/g)
Carbohydrate	17.1
Fat	39.5
Protein	14

- *25.44** Under what circumstances would the heat of formation and the heat of combustion have the same value?
- **25.45** One of the ways to destroy chlorinated hydrocarbons in waste streams is to add a fuel (here toluene waste), and burn the mixture. In a test of the combustion apparatus, 1200 lb of a liquid mixture composed of 0.0487% hexachloroethane (C_2Cl_6), 0.0503% tetrachloroethane (C_2Cl_4), 0.2952% chlorobenzene (C_6H_5Cl), and the balance toluene was burned completely with air. What was the HHV of the mixture calculated using data for the heats of combustion in Btu/lb? Compare the resulting value with the one obtained from the DuLong formula. The observed value was 15,200 Btu/lb. What is one major problem with the incineration process described above?
- *25.46** Gasohol is a mixture of ethanol and gasoline used to increase the oxygen content of fuels, and thus reduce pollutants from automobile exhaust. What is the heat of reaction for one kg of the mixture calculated using heat of combustion data for a fuel comprised of 10% ethanol and the rest octane? How much is the heat of reaction reduced by adding the 10% ethanol to the octane?
- **25.47** Yeast cells can be grown in a culture in which glucose is the sole source of carbon to produce cells that are up to 50% by weight of the glucose consumed. Assume the following chemical reaction equation represents the process:



The formula for glucose is $C_6H_{12}O_6$, hence CH_2O is directly proportional to one mole of glucose. Given the following data for the heat of combustion:

	$\Delta \hat{H}_c^\circ$ (kJ/g mol)	MW
Dry cells ($C_{3.92}H_{6.5}O_{1.94}$)	-1,517	84.58
Glucose (CH_2O)	-2,817	30.02

calculate the standard heat of reaction per 100 g of dry cells.

- *25.48** The composition of a strain of yeast cells is determined to be $C_{3.92}H_{6.5}O_{1.94}$, and the heat of combustion was found to be $-1,518$ kJ/g mol yeast. Calculate the heat of formation of 100 g of the yeast.

CHAPTER 26

ENERGY BALANCES THAT INCLUDE THE EFFECTS OF CHEMICAL REACTION

26.1 Analysis of the Degrees of Freedom to Include the Energy Balance with Reaction	803
26.2 Applications of Energy Balances in Processes that Include Reactions	806

Your objectives in studying this chapter are to be able to:

1. Apply the general energy balance to open and closed systems involving both complete and incomplete reactions.
2. Given information on the moles or mass, temperature, and/or compositions of the process inputs, compute the moles or mass, temperature, and/or compositions of the outputs.
3. Calculate the adiabatic reaction temperature.
4. Determine the temperature of an incoming stream of material given the exit stream temperature (when a reaction occurs), or the reverse.
5. Calculate how much material must be introduced into a system to provide a prespecified quantity of heat transfer for the system.
6. Carry out a degree-of-freedom analysis that includes the energy balance with reactions occurring.

You have at this point reached the culmination of both mass and energy balances. It is now time to apply your skills and tools to more complex processes than those we have used in prior chapters.

Looking Ahead

In this chapter we first examine how to expand the degree-of-freedom analysis to include energy balances with reaction. Then we proceed to go through four problems involving three different industrial processes that you can use to compare your

problem-solving skills with the solution presented. If you cover up the solution first and look at it only after analyzing the problem, you will get the most benefit from this chapter.

26.1 Analysis of the Degrees of Freedom Including the Energy Balance with Reaction

*You propound a complicated mathematical problem: give me
a slate and half an hour's time, and I can produce a wrong answer.*

George Bernard Shaw

Chapter 10 described how to carry out a degree-of-freedom analysis in a problem involving chemical reactions. The inclusion of energy balances involves a simple extension of the count of the unknowns and equations. One extra equation is involved: the energy balance equation. What additional variables do you have to take into account? You have to take into account the variables in the energy balance, which usually simplify to just the temperature and pressure of all of the streams, and the amount of heat transferred to or from the system. You can make just one energy balance for a designated system, but each of the terms in the energy balance adds one or more additional variables to the set of variables that must be considered in the analysis. Fortunately, most of the terms in the energy balance will be specified or implied as being zero, such as the PE , KE , or W , because in the majority of problems the energy balance is applied to a open, steady-state system for which $Q = \Delta H$.

Do you recall from Chapter 21 and subsequent discussion that the enthalpy is a function of temperature and pressure? Thus, in a degree-of-freedom analysis you usually replace one variable, the enthalpy of a stream with two variables, the temperature and pressure. (If the process is unsteady state, you might replace the internal energy inside the system with temperature and specific volume instead of the temperature and pressure.)

If the material balances and other equations, such as specifications and equilibrium relations, can be solved separately from the energy balance (i.e., decoupled from the energy balance), then you can complete the degree-of-freedom analysis for the material balances separately from the degree-of-freedom analysis for the energy balance. If not, then the degree-of-freedom analysis will have to include the variables associated with both the material and energy balances, as shown in Table 26.1. We use only relatively simple problems in this book, but the analysis of a system in a typical industrial plant might involve hundreds of variables and equations so that you can easily make some errors in your accounting, and arrive at an incorrect value for the degrees of freedom. You might miss or forget some variables, or write some equations that are not independent. Refer to Chapter 30 for more detailed informa-

TABLE 26.1 Degree-of-Freedom Analysis for a Steady-State Flow System*Types of variables involved*

- Temperature of a stream
- Pressure of a stream
- Species flow in a stream, or composition of a stream plus total flow
- Extent of reaction

Types of equations used

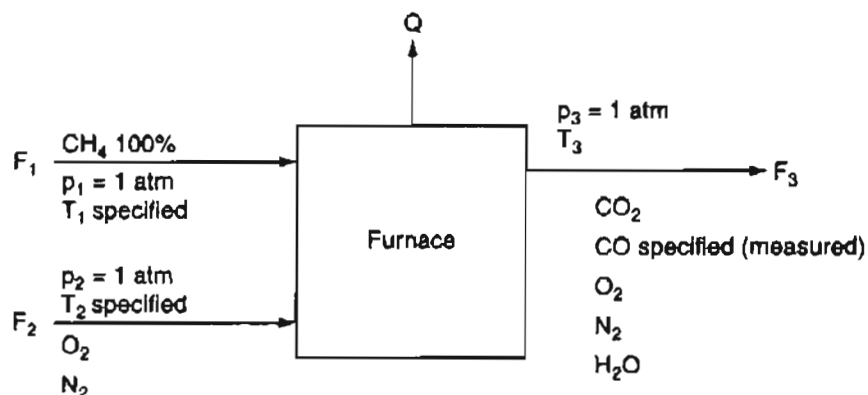
- Independent material balances
- Energy balance
- Phase equilibrium relations
- Chemical equilibrium relations
- Variables with specified values
- Conversion or extent of reaction specified
- Heat flow (and work) specified
- Recycle ratio specified

tion about the degree-of-freedom analysis for the simultaneous solution of material and energy balances. Fortunately, commercial steady-state flowsheeting and optimization software (refer to Chapter 31) include tools to simplify the application of a degree-of-freedom analysis to complex systems.

The following example illustrates a degree-of-freedom analysis that includes an energy balance when a reaction occurs.

EXAMPLE 26.1 Analysis of the Degrees of Freedom for a Combustion Process

Methane is burned with 5% excess air in a furnace. Figure E26.1 shows the stream compositions and those variables whose values are specified. The process occurs with each stream at 1 atm. Determine if the number of degrees of freedom for the process is zero.

**Figure E26.1**

Solution

You should make a table to help in the count of the variables and equations. The energy balance is assumed to reduce to $Q = \Delta H$; replace ΔH as a variable with p and T .

Number of variables in the process (ignoring those with zero value):

Species in F_1	1	
F_2	2	
F_3	<u>5</u>	8
Total stream flows		3
Stream temperatures		3
Stream pressures		3
Q		1
Extent of reaction (2 reactions)		2
Total		<u>20</u>

Number of equations:

Independent species material balances	6
Sum of species in each of the 2 streams ($\sum n_i^j = F_j$)	2
Energy balance	1
Specification of the value of a variable	
Total stream flows (F_1 , the basis, and F_2 comes from 5% excess air)	2
Species values (CO)	1
Pressures ($p_1 = p_2 = p_3 = 1$ atm)	3
Temperatures (T_1 and T_2)	2
O_2 to N_2 ratio specified in F_2 (an implicit specification)	1
Complete reaction (no CH_4 in exit stream exists) hence the extent of reaction is implied for both reactions (to CO and CO_2)	<u>2</u>
Thus, the degrees of freedom are zero	<u>20</u>

If you include the Ar in the air that enters with the O_2 and N_2 so that Ar appears in the exit gas from the furnace, how will the degree-of-freedom analysis be affected? Hints: (a) Does Ar react? (b) Is the Ar entering specified? How would the analysis above change if you used element instead of species material balances?

SELF-ASSESSMENT TEST**Questions**

1. Can you make a degree-of-freedom analysis if you do not know the specific reaction equations for a process in which a reaction takes place?
2. If the temperatures of the flow streams are given but not the pressures, how do you treat the pressures in a degree-of-freedom analysis, that is, do you include or exclude them?
3. Can the degree-of-freedom analysis when carried out separately for the material balances and energy balances give results that differ from the degree-of-freedom analysis for the combined material and energy balances?

Problems

1. Acetic acid (CH_3COOH) at 350°F is decomposed in a steady-state flow reaction at 450°F so that gaseous ketene (CH_2CO) and methane (CH_4) are produced. The by-products are $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. Measurements show that 68.2% total conversion of the acetic acid occurs and that the conversion to ketene is 9.3%. Prepare an analysis of the degrees of freedom for this process to determine the number of additional specifications that must be provided to obtain zero degrees of freedom. Hint: Do you know the exit gas temperature?
2. In the contact process SO_2 is converted to SO_3 in a nonadiabatic reactor. If the mole fractions of entering gas, which consists of SO_2 , O_2 , and N_2 , are known, if the outlet gas is comprised of SO_2 , SO_3 , O_2 , and N_2 , if the molar flow rates of the entering and exiting gases are known, and the entering temperature and entering and exiting pressure of the streams are known, what are the degrees of freedom in this problem for a conversion of the SO_2 of 80%? Will the degrees of freedom calculated for 80% conversion change if the conversion drops to 70%?

26.2 Applications of Energy Balances in Processes that Include Reactions

My method to overcome a difficulty is to go round it.

George Pólya

In this section we primarily illustrate the solution of continuous, steady-state processes for which the general energy balance reduces to two choices:

- With the effects of chemical reaction merged with the sensible heats

$$\begin{aligned} Q &= \Delta H = [H(T) - H(25^\circ\text{C})]_{\text{outputs}} - [H(T) - H(25^\circ\text{C})]_{\text{inputs}} \quad (26.1a) \\ &= \Delta H_{\text{outputs}} - \Delta H_{\text{inputs}} \end{aligned}$$

- With the effects of chemical reaction lumped in the heat of reaction

$$\begin{aligned} Q &= [H(T) - H(25^\circ\text{C})]_{\text{outputs}}^{\text{sensible} + \text{phase change}} - [H(T) - H(25^\circ\text{C})]_{\text{inputs}}^{\text{sensible} + \text{phase change}} \\ &\quad + \Delta H_{\text{rxn}} \quad (26.1b) \end{aligned}$$

We will use Equation (26.1a) in the examples below.

Here are some typical problems frequently posed for open systems:

1. What is the temperature of one stream given data for the other streams?
2. How much heat has to be added to or removed from the process?
3. What is the temperature of the reaction?
4. How much material must be added or removed from the process to give a specified value of heat transfer?

You can think of many others.

A topic related to question #1 above pertains to a special term called the **adiabatic reaction (theoretical flame, combustion) temperature**, which is defined as the temperature obtained inside the process when

1. the reaction is carried out under adiabatic conditions, that is, there is no heat interchange between the vessel in which the reaction is taking place and the surroundings;
2. no other effects occur, such as electrical effects, work, ionization, free radical formation, and so on; and
3. the limiting reactant reacts completely.

We assume that the products leave at the temperature of the reaction, and thus if you know the temperature of the products, you automatically know the temperature of the reaction.

When you calculate the adiabatic reaction temperatures for combustion reactions, you assume complete combustion occurs, but equilibrium considerations may dictate less than complete combustion in practice. For example, the adiabatic flame temperature for the combustion of CH_4 with theoretical air has been calculated to be 2010°C ; allowing for incomplete combustion, it would be 1920°C . The actual temperature when measured is 1885°C .

The adiabatic reaction temperature tells you the temperature ceiling of a process. You can do no better, but of course the actual temperature may be less. The adiabatic reaction temperature helps you select the types of materials that must be specified for the equipment in which the reaction is taking place. Chemical combustion with air produces gases with a maximum temperature of 2500 K, but the temperature can be increased to 3000 K with the use of oxygen and more exotic oxidants, and even this value can be exceeded, although handling and safety problems are severe. Applications of such hot gases lie in the preparation of new materials, micromachining, welding using laser beams, and the direct generation of electricity using ionized gases as the driving fluid.

The steady-state energy balance with $Q = 0$ reduces to just $\Delta H = 0$. If you use tables such as in Appendix D rather than heat capacity equations to calculate the "sensible heats" of the various streams entering and leaving the reactor, the calculations will involve trial and error. To find the exit temperature for which $\Delta H = 0$, if tables are used as the source of the $\hat{\Delta H}$ values, the simplest procedure is to

1. Assume a sequence of values of T selected to bracket $\Delta H = 0$ (+ and -) for the sum of the enthalpies of the outputs minus the enthalpies of the inputs.
2. Once the bracket is obtained, interpolate within the bracket to get the desired value of T when $\Delta H = 0$.

Don't forget to subtract the value of the enthalpy at 25°C from the value of the enthalpy in the tables if the reference temperature for the tables is 0°C . If you integrate

the heat capacity equations to obtain the sensible heats, you will formulate a cubic or quadratic equation to be solved for the exit temperature.

For an unsteady-state *closed system* with ΔKE and $\Delta PE = 0$ inside the system and $W = 0$, the energy balance becomes

$$Q = \Delta U = U_{\text{final}} - U_{\text{initial}} \quad (26.2)$$

If you do not have values for $\Delta \hat{U}$, you have to calculate ΔU from $\Delta H - \Delta(pV)$ in which the heats of formation are meshed with the sensible heats and phase changes

$$Q = [H(T) - H(25^\circ\text{C})]_{\text{final}} - [H(T) - H(25^\circ\text{C})]_{\text{initial}} - [(pV)_{\text{final}} - (pV)_{\text{initial}}] \quad (26.3)$$

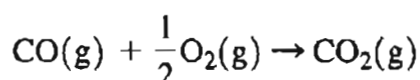
The contribution of $\Delta(pV)$ is frequently negligible. For a constant volume process, $\Delta(pV) = V\Delta p$, and for a constant pressure but expandable closed system $\Delta(pV) = p\Delta V$. For the special case of an ideal gas, $\Delta(pV) = \Delta(nRT) = R\Delta(nT)$.

EXAMPLE 26.2 Calculation of an Adiabatic Reaction (Flame) Temperature

Calculate the theoretical flame temperature for CO gas burned at constant pressure with 100% excess air, when the reactants enter at 100°C and one atm.

Solution

The solution presentation will be compressed to save space. The system is shown in Figure E26.2. We will use data from the Appendix and the CD in the back of this book. The process is a steady-state flow system. Ignore any equilibrium effects.



Basis: 1 g mol of CO(g); ref. Temp. 25°C and 1 atm

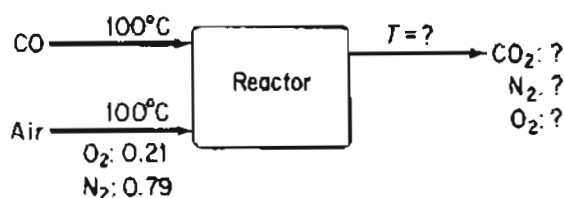


Figure E26.2

The reaction is always assumed to occur with the limiting reactant completely reacting. The excess air is a nonreacting component, but requires sensible heat to

raise its temperature to the adiabatic reaction temperature. We will use the method of meshing all of the pertinent enthalpy changes for each compound entering and leaving the system. You can solve the material balances (for which the degrees of freedom are zero) independently of the energy balance. A summary of the results of the solution of the material balances is:

Entering compounds		Exit compounds	
Component	g mol	Component	g mol
CO(g)	1.00	CO ₂ (g)	1.00
O ₂ (req. + xs)		O ₂ (g)	0.50
0.50 + 0.50	1.00	N ₂ (g)	3.76
N ₂	3.76		
(Air = 4.76)			

Select the reference state to be 25°C and 1 atm. In the first approach to the solution of the problem, the “sensible heat” (enthalpy) values have been taken from the table of the enthalpy values for the combustion gases in Appendix D. They could not be calculated using the physical property software on the accompanying CD as the states at 1000 K are out of range. The energy balance (with $Q = 0$) reduces to $\Delta H = 0$. Here is the data needed for the energy balance.

Component	g mol	T(K)	$\Delta \hat{H}$ (J/g mol)	$\Delta \hat{H}_f^\circ$ (J/g mol)	ΔH (J)
<i>Inputs</i>					
CO	1.00	373	(2917–728)	–110,520	–108,331
O ₂	1.0	373	(2953–732)	0	2,221
N ₂	3.76	373	(2914–728)	0	8,219
		Total			–97,891
<i>Outputs</i>					
Assume T = 2000K:					
CO ₂	1.00	2000	(92,466–912)	–393,510	–301,956
O ₂	0.50	2000	(59,914–732)	0	29,591
N ₂	3.76	2000	(56,902–728)	0	211,214
		Total			–61,151

$$\Delta H = \Delta H_{\text{outputs}} - \Delta H_{\text{inputs}} = (-61,151) - (-97,891) = 36,740 > 0$$

Assume T = 1750K:

CO ₂	1.00	1750	(77,455–912)	–393,510	–316,977
O ₂	0.50	1750	(50,555–732)	0	24,912
N ₂	3.76	1750	(47,940–728)	0	177,517
		Total			–114,548

$$\Delta H = (-114,548) - (-97,891) = -16,657 < 0$$

Now that $\Delta H = 0$ is bracketed, we can carry out a linear interpolation to find the theoretical flame temperature (TFT):

$$\text{TFT} = 1750 + \frac{0 - (-16,657)}{36,740 - (-16,657)}(250) = 1750 + 78 = 1828\text{K} (1555^\circ\text{C})$$

An alternate approach to solving this problem would be to develop explicit equations in TFT to be solved for TFT without trial and error. The difference from the first approach is that you would have to formulate nonlinear polynomial equations in TFT by integrating the heat capacity equations for each compound to obtain the respective sensible heats for each compound. If the heat capacity equations were cubic in T , the integrated equations in TFT would be quartic. You can take the integrated equations for each compound from the CD that accompanies this book to avoid error, introduce them into the energy balance as sensible heats, merge them, and solve the resulting energy balance using an equation solver such as Polymath. You can get a rough preliminary solution by truncating the quartic equations to quadratic equations, and solve the latter.

Suppose the process shown in Figure E26.2 were changed to a closed system in which stoichiometric amounts of CO and O₂ react to produce CO₂. What do you do to solve the revised problem? You use equation (26.3) with $Q = 0$. Will the TFT be different? Yes.

$$\Delta H_{\text{inputs}} = -97,891 \text{ J}$$

Assume $T = 1500 \text{ K}$. Then $\Delta H_{\text{outputs}}$ is

Component	g mol	$T(\text{K})$	$\Delta \hat{H}(\text{J/g mol})$	$\Delta \hat{H}_f^\circ(\text{J/g mol})$	$\Delta H(\text{J})$
CO ₂	1.00	1500	(62,676 - 912)	-393,510	-331,764
O ₂	0.50	1500	(41,337 - 732)		20,303
N ₂	3.76	1500	(39,145 - 728)		144,478
Total				-166,996	

To avoid making real gas calculation, let's assume that the entering and exit gases are ideal (you can calculate z if you want—you will find it close to 1) so that

$$\Delta(pV) = R\Delta(nT) = R(n_2T_2 - n_1T_1)$$

$$n_2 = 5.26 \quad n_1 = 5.76 \quad T_2 = T \text{ K} \quad T_1 = 298 \text{ K}$$

$$R(n_2T_2 - n_1T_1) = \frac{8.314 \text{ J}}{(\text{g mol})(\text{K})} \left| \frac{(5.76)(298) - (5.26T)(\text{g mol})(\text{K})}{(\text{g mol})(\text{K})} \right|$$

$$= 14,271 - 43.73 T$$

$T(\text{K})$	$R\Delta(nT) \text{ J}$
2000	-73,189
1750	-62,257
1500	-51,324

The energy balance is

$$\text{At } 1750 \text{ K: } (-114,548) - (-97,891) - (62,657) = 46,000 > 0$$

$$\text{At } 1500 \text{ K: } (-166,991) - (-97,891) - (-51,324) = -17,776 < 0$$

Linear interpolation gives

$$\text{TFT} = 1500 + \frac{0 - (-17,776)}{46,000 - (-17,776)}(250) = 1570 \text{ K}$$

EXAMPLE 26.3 Application of the General Energy Balance in a Process in which More Than One Reaction Occurs

Limestone (CaCO_3) is converted to calcium oxide (CaO) in a continuous vertical kiln as illustrated in Figure E26.3a. The energy to decompose the limestone is supplied by the combustion of natural gas (CH_4) in direct contact with the limestone using 50% excess air. The CaCO_3 enters the process at 25°C and the CaO exits at 900°C . The CH_4 enters at 25°C and the product gases exit at 500°C . Calculate the number of pounds of CaCO_3 that can be processed per 1000 ft^3 of CH_4 measured at standard conditions. To simplify the calculations, assume that the heat capacities of CaCO_3 ($56.0 \text{ Btu}/(\text{lb mol})(^\circ\text{F})$) and CaO ($26.7 \text{ Btu}/(\text{lb mol})(^\circ\text{F})$) are constant.

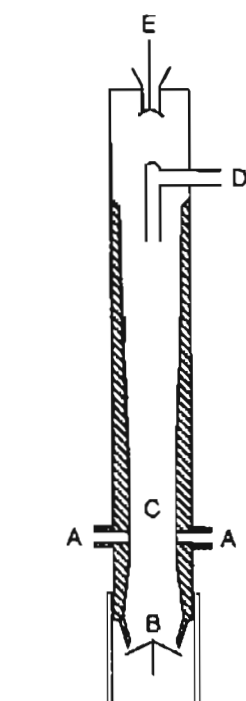


Figure E26.3a

Figure E26.3a shows a vertical line kiln comprised of a steel cylinder lined with fire brick approximately 80 ft high and 10 ft in diameter. Fuel is supplied at A, air at B, and limestone (CaCO_3) at E. Combustion products and CO_2 exit at D.

Solution

In this problem the material and energy balances are coupled and must be solved simultaneously. The process is open and steady state.

Steps 1, 2, and 3

You have to decide whether to make the calculations using the SI or AE systems of units. We will use the SI system for most of the solution for convenience, but the CD in the back of this book makes use of the AE system just as easy. We will assume that the entire process occurs at 1 atm and that the air enters at 25°C.

You have to make some preliminary calculations to carry out a material balance. To do so you have to choose a basis.

Step 5

Let us start with a basis of 1 g mol CH₄ for convenience. Many other bases could be selected.

Steps 3 and 4

The heat capacities of CaCO₃ and CaO, respectively, in kJ/g mole are:

CaCO ₃	0.130 kJ/g mol	MW = 100.09
CaO	0.062 kJ/g mol	MW = 56.08

The reactions are

- (a) $\text{CaCO}_3 (\text{s}, 25^\circ\text{C}) \rightarrow \text{CaO} (\text{s}, 900^\circ\text{C}) + \text{CO}_2 (\text{g}, 500^\circ\text{C})$
 (b) $\text{CH}_4 (\text{g}, 25^\circ\text{C}) + 2\text{O}_2 (\text{g}, 25^\circ\text{C}) \rightarrow \text{CO}_2 (\text{g}, 500^\circ\text{C}) + 2\text{H}_2\text{O} (\text{g}, 500^\circ\text{C})$

The moles of O₂ and N₂ entering are

1 mol CH ₄ requires:	2 g mol O ₂
50% excess:	$\frac{1}{3}$
Total O ₂	3
Entering N ₂ :	$3 (0.79/0.21) = 11.29 \text{ g mol}$

You can use Figure E26.3b as a guide for the material and energy balances.

Steps 6 and 7

To make a degree-of-freedom analysis for the material balances you have to count the unknowns and equations. Based on an analysis using species:

The number of unknowns is 13 (ignoring the variables whose values are zero):

$$n_{\text{CO}_2}^G, n_{\text{O}_2}^G, n_{\text{N}_2}^G, n_{\text{H}_2\text{O}}^G, n_{\text{O}_2}^A, n_{\text{N}_2}^A, P, G, L, M, A, \xi_a, \xi_b$$

The number of independent equations is 12:

- (a) Species balances

CaCO₃, CaO, CH₄, CO₂, O₂, N₂, H₂O

- (b) Specification of 50% excess air

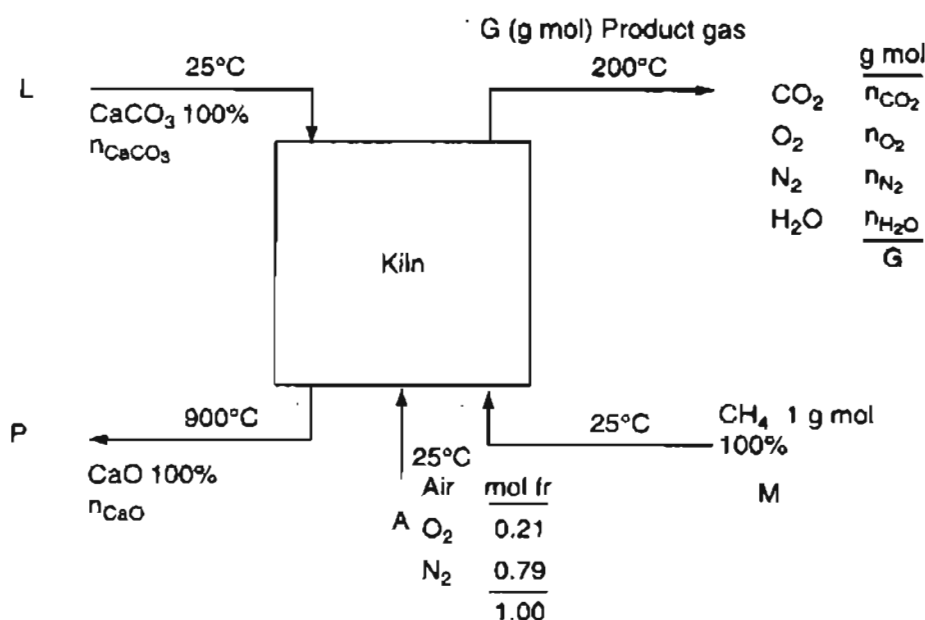


Figure E26.3b

(c) Sum of components in G and A	2
(d) Implied complete reaction (b)—no CH_4 in G	1
(e) Basis selection ($M = 1$)	1
	<hr/> 12

The degrees of freedom are -1 .

From the viewpoint of a degree of freedom analysis based on using element balances, the number of unknowns is reduced by two (the extents of reaction are not involved), and the number of material balances is also reduced by two (5 elements vs. 7 species). The degrees of freedom are still -1 . We will use element balances in solving this problem.

Note that specification of complete reaction for reaction (b) would be redundant with the implicit specification of 0% CaO in L and 0% CaCO_3 in P . Thus, the degrees of freedom are -1 , and to solve the problem you have to include an energy balance. If we can assume $Q = 0$ approximately, the energy balance reduces to $\Delta H = 0$.

Steps 8 and 9

The element material balances reduce to in = out.

Balance	In	=	Out	
C:	$1 + L$	=	$n_{\text{CO}_2}^G$	(1)
2N:	11.29	=	$n_{\text{N}_2}^G$	(2)
H:	4 (1)	=	$2n_{\text{H}_2\text{O}}^G$ hence $n_{\text{H}_2\text{O}}^G = 2$	(3)
O:	$3L + 2(3)$	=	$2n_{\text{CO}_2}^G + 2n_{\text{O}_2}^G + n_{\text{H}_2\text{O}}^G + P$	(4)
Ca:	L	=	P	(5)

If you eliminate Equations (2) and (3) for which the solution is given, you get a reduced set of 3 equations in 4 unknowns.

Steps 4 and 8

To write an energy balance you need to get data on all of the heats of formation of the respective species and the enthalpies for the “sensible” heats.

We will combine the heats of formation with sensible heat data from the software on the CD that accompanies this book. The values for the heats of formation of the solid species are from Appendix F.

Species	g mol	$T(^{\circ}\text{C})$	$\Delta\hat{H}_f^{\circ}(\text{kJ/g mol})$	Sensible heats $\Delta\hat{H}_f^{\circ}(\text{kJ/g mol})$	Stream $\Delta H(\text{kJ})$
<i>Out</i>					
$\text{CO}_2(\text{g})$	$n_{\text{CO}_2}^G$	500	-393.250	21.425	$-371.825n_{\text{CO}_2}^G$
$\text{O}_2(\text{g})$	1	500	0	15.034	15.034
$\text{N}_2(\text{g})$	11.29	500	0	14.241	160.781
$\text{H}_2\text{O}(\text{g})$	2	500	-241.835	17.010	-449.650
$\text{CaO}(\text{s})$	P	900	-635.6	$(0.062)(100-25)$	$-581.35P$
<i>In</i>					
$\text{CH}_4(\text{g})$	1	25	-49.963	0	-49.963
$\text{CaCO}_3(\text{s})$	L	25	-1206.9	0	$-1206.9L$
$\text{O}_2(\text{g})$	3	25	0	0	0
$\text{N}_2(\text{g})$	11.29	25	0	0	0

We have assumed $Q = 0$. If you know the temperature distribution at the wall of the kiln you could calculate Q , but the information is not given in the problem. Thus, the energy balance is with ($P = L$)

$$\begin{aligned} -371.825n_{\text{CO}_2}^G + 15.304 + 160.781 - 449.650 - 581.350L \\ = -49.963 - 1206.9L \end{aligned} \quad (6)$$

Solve Equation (1) and (6) simultaneously to get

$$L = 2.56 \text{ g mol}$$

On the basis of 1 g mol CH_4

$$\frac{2.56 \text{ g mol CaCO}_3}{1 \text{ g mol CH}_4} \bigg| \frac{100.09 \text{ g CaCO}_3}{1 \text{ g mol CaCO}_3} = \frac{256 \text{ g CaCO}_3}{1 \text{ g mol CH}_4}$$

To get the ratio asked for (assuming CH_4 is an ideal gas—a good assumption)

$$\frac{1000 \text{ ft}^3 \text{ CH}_4}{359.05 \text{ ft}^3} \bigg| \frac{1 \text{ lb mol}}{1 \text{ lb mol CH}_4} \bigg| \frac{256 \text{ lb CaCO}_3}{1 \text{ lb mol CaCO}_3} = \frac{713 \text{ lb CaCO}_3}{1000 \text{ ft}^3 \text{ CH}_4 \text{ at SC}}$$

If you decided to use the exit gas from the kiln to preheat the entering air, would you increase or decrease the ratio calculated above? Hint: The exit gases from the entire system including the heat exchange would be at a lower temperature. What would that do to the sensible heats of the exit gases?

EXAMPLE 26.4 Application of the Energy Balance to a Process Composed of Multiple Units

Figure E26.4a shows a process in which CO is burned with 80% of the theoretical air in Reactor 1. The combustion gases are used to generate steam, and also to transfer heat to the reactants in Reactor 2. A portion of the combustion gases that are used to heat the set of tubes in Reactor 2 are recycled. SO₂ is oxidized in Reactor 2. You are asked to calculate the lb mol of CO burned per hour in Reactor 1. Note: The gases involved in the SO₂ oxidation do not come in direct contact with the combustion gas used to heat the SO₂ reactants and products.

Data for Reactor 2 pertinent to the SO₂ oxidation is

Reactants	mol fr.	T °F
SO ₂	0.667	77
O ₂	0.333	77
	1.00	
Products		
SO ₃	0.586	1000
SO ₂	0.276	1000
O ₂	0.138	1000
	1.000	

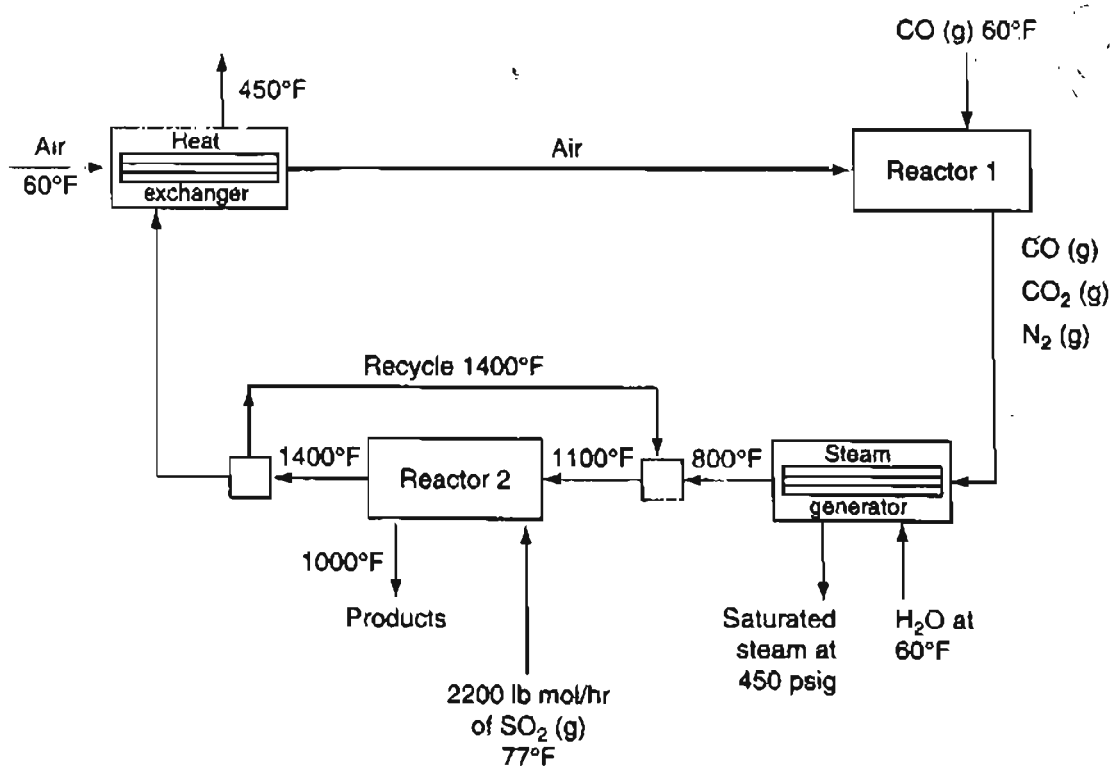


Figure E26.4a

Solution

A number of key decisions must be made before starting any calculations to solve this problem.

1. What units should you use? Although all of the data in the diagram are in the AE system, the convenient enthalpy data are in the SI system, hence we will use the latter. The temperature conversions are:

T(°F)	T(K)
77	298
800	700
1000	811
1400	1033

2. What system should you choose to start with in the calculations? This phase of the analysis involves Steps 6 and 7 of the strategy covered in Chapter 7. Selection of the entire process as the system will lead to about 15 unknowns and require 15 independent equations. It makes sense to look for a system involving fewer unknowns and equations. If you examine each subsystem in the process, the selection of Reactor 2 excluding the recycle stream proves to be a reasonable choice. It includes SO_2 directly, and the input and output temperatures are known.
3. What basis should be used? The given amount of material is the 2200 lb mol/hr of SO_2 . A convenient basis would be 1 g mol of CO entering. Both bases are suitable—we will use the latter, and at the end of the calculations convert to a basis of lb mol of CO per hour.

In addition to the three decisions listed above, you have to make some assumptions:

1. The process is a continuous flow process, hence $\Delta E = 0$
2. The pressure everywhere is 1 atm.
3. No heat loss occurs ($Q = 0$ in the energy balances)
4. $\Delta KE = \Delta PE = W = 0$

Step 5

Basis: 1 g mol CO entering Reactor 1

Step 2

A figure helps in the analysis—examine Figure E26.4b. The system is Reactor 2 excluding the recycle stream.

Step 3

On the selected basis you have to calculate the O_2 , N_2 , CO, and CO_2 in the combustion gases from Reactor 1 that pass through the entire process. No O_2 exists in the combustion products because no excess air is used. Thus, the combustion gases calculations are:

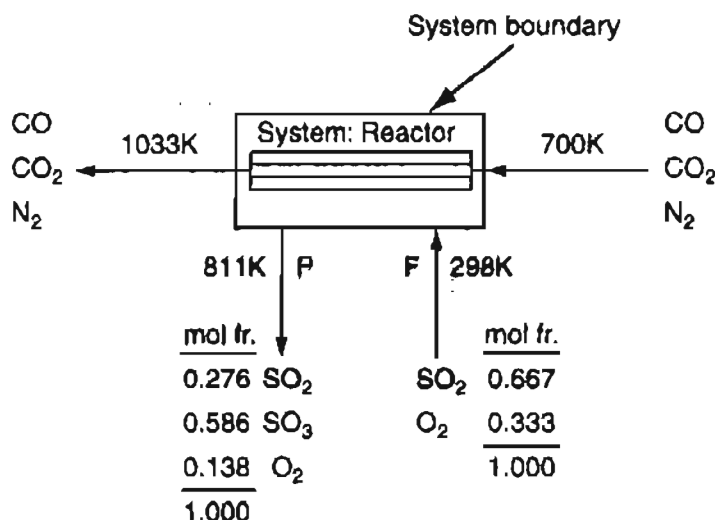
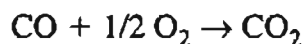


Figure E26.4b

Basis: 1 g mol CO(g) entering Reactor 1



Entering O₂: 1 (0.5)(0.8) = 0.4 g mol

Entering N₂: 0.4 (79/21) = 1.5 g mol

Summary of the output of Reactor 1

Component	g mol	mol fr.
CO	1(1-0.8) = 0.2	0.32
CO ₂	1(0.8) = 0.8	0.08
N ₂	= 1.5	0.60
Total	2.5	1.00

Steps 6 and 7

The degree-of-freedom analysis is as follows.

The number of *unknowns* in the system in Figure E26.4b are 8: $n_{\text{SO}_2}^F, n_{\text{O}_2}^F, n_{\text{SO}_2}^P, n_{\text{SO}_3}^P, n_{\text{O}_2}^P, \xi, F$, and P . How many *independent equations* are there?

A typical analysis would be as follows:

- | | |
|--|--------|
| (a) SO ₂ , SO ₃ , and O ₂ balances | 3 |
| (b) two sum of mole fractions $\sum \omega_i = 1$ | 2 |
| (c) independent specifications of the values of mole fractions:
2 in P and 1 in F | 3
8 |

But the analysis is not correct! Why? Only two of the three species balances are independent. Suppose you write the equations.

Steps 8 and 9

The three species balances are

$$\text{SO}_2: \quad P(0.276) - F(0.667) = -1(\xi) \quad (\text{a})$$

$$\text{SO}_3: \quad P(0.586) - F(0) = 1(\xi) \quad (\text{b})$$

$$\text{O}_2: \quad P(0.138) - F(0.333) = -0.5(\xi) \quad (\text{c})$$

Because Equations (a) to (c) are a set of homogeneous equations $f(x) = 0$, that is, when each equation is rearranged and set equal zero, every term is associated with a variable. As pointed out in Appendix L1, no nontrivial solution exists. Try to solve Equations (a)–(c), and you will see this condition is true. Thus, one more equation is needed. What equation can you use? What is the topic of this chapter! Use an energy balance.

For you to make an energy balance you have to get information about the heats of formation and the sensible heats. The data used below have been taken from the CD in the back of this book. With the assumptions made, the energy balance reduces to $\Delta H = 0$.

Data and Calculations for the Energy Balance

Comp	g mol	T(K)	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	$\Delta \hat{H}_{\text{sensible}}$ (kJ/g mol)	ΔH (kJ)
Out					
CO(g)	0.2	1033	-109.054	35.332	-14.744
CO ₂ (g)	0.8	1033	-393.250	35.178	-286.458
N ₂ (g)	1.5	1033	0	22.540	33.810
SO ₂ (g)	$n_{\text{SO}_2}^P$	811	-296.855	20.845	$-276.010n_{\text{SO}_2}^P$
SO ₃ (g)	$n_{\text{SO}_3}^P$	811	-395.263	34.302	$-360.961n_{\text{SO}_3}^P$
O ₂ (g)	$n_{\text{O}_2}^P$	811	0	16.313	$16.313n_{\text{O}_2}^P$
In					
CO(g)	0.2	700	-109.054	17.177	-18.375
CO ₂ (g)	0.8	700	-393.250	17.753	-300.398
N ₂ (g)	1.5	700	0	11.981	17.972
SO ₂ (g)	$n_{\text{SO}_2}^F$	298	-296.855	0	$-296.855n_{\text{SO}_2}^F$
O ₂ (g)	$n_{\text{O}_2}^F$	298	0	0	0

The energy balance is

$$-276.010n_{\text{SO}_2}^P - 360.961n_{\text{SO}_3}^P + 296.855n_{\text{SO}_2}^F + 16.313n_{\text{O}_2}^P = -33.41n_{\text{SO}_2}^F \quad (\text{d})$$

Step 9

Substitute for the variables in Equation (d) the following to get Equation (d) in terms of F and P :

$$\begin{aligned} n_{\text{SO}_2}^P &= P(0.276) & n_{\text{O}_2}^P &= P(0.138) \\ n_{\text{SO}_3}^P &= P(0.586) & n_{\text{SO}_2}^F &= F(0.667) \end{aligned}$$

Solve Equation (d) in terms of F and P together with Equations (a) and (b) (using Polymath) to get (the n_i are in g mol)

$$n_{\text{SO}_2}^P = 0.312 \quad n_{\text{SO}_2}^F = 0.974$$

$$n_{\text{SO}_3}^P = 0.662 \quad n_{\text{O}_2}^F = 0.486$$

$$n_{\text{O}_2}^P = 0.156$$

$$P = 1.13 \quad \xi = 0.66$$

$$F = 1.46$$

Step 10

Check the solution using an oxygen balance

$$\text{O: } 2n_{\text{SO}_2}^P + 3n_{\text{SO}_3}^P + 2n_{\text{O}_2}^P - 2n_{\text{O}_2}^F - 2n_{\text{SO}_2}^F = 0$$

$$2(0.312) + 3(0.662) + 2(0.156) - 2(0.486) - 2(0.974) = 0$$

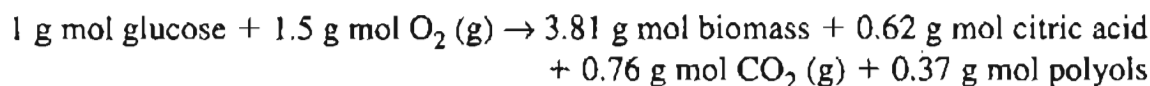
Finally, you need to calculate the lb mol of CO/hr that flow into Reactor 1. Because no loss of combustion gases occurs up to and through Reactor 2, you know (on the basis of 1 g mol CO entering Reactor 1) that

$$\frac{1 \text{ lb mol CO}}{0.974 \text{ lb mol SO}_2} \left| \frac{2200 \text{ lb mol SO}_2}{\text{hr}} \right| = 2259 \frac{\text{lb mol CO}}{\text{hr}}$$

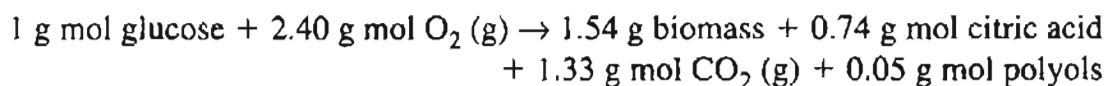
EXAMPLE 26.5 Production of Citric Acid by a Fungus

Citric acid is a well known compound that occurs in living cells for both plants and animals. The citric acid cycle is a series of chemical reactions occurring in living cells that is essential for the oxidation of glucose, a major source of energy for the cells. The reaction scheme is far too complicated to show here, but from a macroscopic (overall) viewpoint, for the commercial production of citric acid in a batch process, three different phases occur for which the stoichiometries are slightly different:

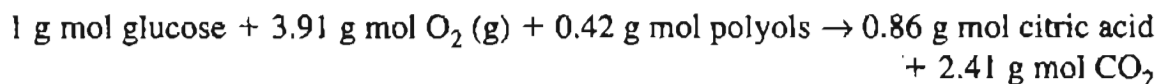
Early idophase (occurs between 80 and 120 hours), initial reaction



Medium idophase (occurs between 120 and 180 hours), additional glucose consumed



Late idophase (occurs between 180 and 220 hours), additional glucose consumed



In an aerobic (in the presence of air) batch process, a 30% glucose solution at 25°C is introduced into a fermentor. Citric acid is to be produced by using the fungus *Aspergillus niger*. Stoichiometric sterile air is mixed with the culture solution by a 100 hp aerator. Only 60% overall of the glucose supplied is expected to be converted to citric acid. The early phase is run at 32°C, the middle phase at 35°C, and the late phase at 25°C.

Based on the given data, how much heat has to be added or removed from the fermentor during the production of a batch of 10,000 kg of citric acid? Ignore any slight effects of solution on the value of the heat of formation.

Data

	MW	$\Delta \hat{H}_f^\circ$ (kJ/g mol)
d, α glucose ($C_6H_{12}O_6$)	180.16	-1266
Citric acid ($C_6H_8O_7$)	192.12	-1544.8
Dry cells (biomass)	28.6	-91.4

Solution

Let citric acid be denoted by CA and the biomass by BM. You can make a material balance for the overall process for which the total net reaction in g mol is



Material balance

Basis: 10,000 kg CA produced

$$\frac{10,000 \text{ kg CA}}{192.12 \text{ kg CA}} \times \frac{1 \text{ kg mol CA}}{1 \text{ kg mol CA}} = 52.05 \text{ kg mol CA produced}$$

$$\begin{aligned} \frac{52.05 \text{ kg mol CA}}{2.22 \text{ kg mol CA}} & \times \frac{3 \text{ kg mol glucose}}{2.22 \text{ kg mol CA}} = \frac{1.00 \text{ kg mol glucose introduced}}{0.60 \text{ kg mol glucose consumed}} \\ & \times \frac{180.16 \text{ kg glucose}}{1 \text{ kg mol glucose}} = \frac{1.00 \text{ kg soln}}{0.30 \text{ kg glucose}} \\ & = 70,400 \text{ kg of 30\% solution introduced} \end{aligned}$$

The water serves as a culture medium and does not enter the overall stoichiometry.

Summary of the material balances:

Component	Initial (kg mol)	Final (kg mol)
Glucose $(70,400)(0.3)/180.16 =$	117.32	46.93
BM $(52.05)(5.35/2.22) =$		125.44
CA		52.05
O ₂ (accumulated) $(117.32)(7.8/3) =$	305.03	
CO ₂ (accumulated) $(117.32)(4.5/3)(0.60) =$		105.59

We will assume that the O_2 and N_2 drawn into the system and the CO_2 and N_2 leaving the system are deemed to be part of the initial state of the system and the final state, respectively, to maintain a closed system.

Energy balance

For the closed system

$$\Delta U = Q + W$$

because the changes in KE and PE inside the system are zero, and no flow occurs in or out of the system. The assumption about no flow is not correct, of course, because gas flows in at temperatures not specified, and flows out at various temperatures. However, if you were to calculate the energy associated with the gas flows, you would find it to be insignificant with respect to the work done on the system and the heat of reaction.

The work done is

$$W = \frac{100 \text{ hp}}{1 \text{ (hp)(s)}} \left| \frac{745.7 \text{ J}}{1 \text{ (hp)(s)}} \right| \frac{220 \text{ hr}}{1 \text{ hr}} \left| \frac{3600 \text{ s}}{1 \text{ hr}} \right| \frac{1 \text{ kJ}}{1000 \text{ J}} = 5.906 \times 10^7 \text{ kJ}$$

Because we do not have value for U for this system, we will have to assume that

$$\Delta U = \Delta H - \Delta(pV) \cong \Delta H \text{ because } \Delta(pV) \text{ is negligible}$$

Then

$$Q = \Delta H - W$$

The next step is to calculate the enthalpy change. The reference temperature will be 25°C . The initial state is 25°C and the final state is also 25°C so that the sensible heats are zero. We will omit including the nitrogen in the energy balance because the nitrogen in equals the nitrogen out.

	Component	kg mol	$\hat{H}_f^\circ(\text{kJ/g mol})$	$\Delta \hat{H}(\text{kJ})$
Initial	Glucose	117.32	-1266	$-148,530 \times 10^3$
	O_2	305.03	0	0
	Total			$-148,530 \times 10^3$
Final	Glucose	46.93	-1266	$-59,410 \times 10^3$
	BM	125.44	-91.4	$-11,470 \times 10^3$
	CA	52.05	-1544.8	$-80,410 \times 10^3$
	CO_2	105.59	-393.51	$-41,550 \times 10^3$
	Total			$-192,840 \times 10^3$

$$\Delta H = [(-192,840) - (-148,530)] \times 10^3 = -44,310 \times 10^3 \text{ kJ}$$

$$Q = -4.43 \times 10^7 - 5.91 \times 10^7 = -1.03 \times 10^8 \text{ kJ (heat removed)}$$

The reward of a thing well done, is to have done it.

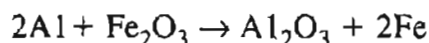
SELF-ASSESSMENT TEST

Questions

1. Why can not the temperature in a combustion reaction exceed the adiabatic reaction temperature?
2. Could the heat of reaction have been used in Example 26.4 rather than the assignment of enthalpies to individual species?
3. Could the heat of combustion have been used in Example 26.4 rather than the assignment of enthalpies to individual species?

Problems

1. A dry low-Btu gas with the analysis of CO: 20%, H₂: 20%, N₂: 60% is burned with 200% excess dry air, which enters at 25°C. If the exit gases leave at 25°C, calculate the heat transfer from the process per unit volume of entering gas measured at standard conditions (25°C and 1 atm).
2. Methane is burned in a furnace with 100% excess dry air to generate steam in a boiler. Both the air and the methane enter the combustion chamber at 500°F and 1 atm, and the products leave the furnace at 2000°F and 1 atm. If the effluent gases contain only CO₂, H₂O, O₂, and N₂, calculate the amount of heat absorbed by the water to make steam per pound of methane burned.
3. A mixture of powdered metallic aluminum and Fe₂O₃ can be used for high-temperature welding. Two pieces of steel are placed end to end, and the powdered mixture is applied between the ends and ignited. If the temperature desired is 3000°F and the heat loss is 20% of ($\Delta H_{\text{prod}} - \Delta H_{\text{react}}$) by radiation, what weight in pounds of the mixture (used in the molecular proportions of 2Al + 1Fe₂O₃) must be used to produce this temperature in 1 lb of steel to be welded? Assume that the starting temperature is 65°F.



	DATA			
	C_p , solid [Btu/(lb)(°F)]	Heat of fusion (Btu/lb)	Melting point (°F)	C_p , Liquid [Btu/(lb)(°F)]
Fe and steel	0.12	86.5	2800	0.25
Al ₂ O ₃	0.20	—	—	—

4. Calculate the theoretical flame temperature when hydrogen burns with 400% excess dry air at 1 atm. The reactants enter at 100°C.

Thought Problems

1. A clipping from the *Wall Street Journal* reads:

Technical Disputes

Furnace efficiency is a comparison of the energy that goes into a furnace with the usable heat that comes out. Because oil furnaces use blowers to burn the fuel more efficiently and because oil produces less water vapor than gas, less heat is vented up the chimney, the Oil Jobbers Council says. The American Gas Association complains that such calculations ignore variations in oil quality that hurt efficiency. And it contends that oil furnaces are apt to "lose efficiency over time," while it says gas furnaces don't.

Which organization is correct, or is neither correct?

2. A review of additives to gasoline to give blends that improve its octane rating shows that oxygenated compounds do not necessarily contain lower energy (Btu per gallon). Acetone, for example, has about the same heat of reaction as does gasoline. It costs 60 cents/gal, whereas unleaded premium gas costs 80 cents/gal (untaxed), so that the result may seem like a standoff. What problems would occur using acetone as a fuel?
3. Degradation of performance and economic loss result from poor boiler performance. What are some of the steps you might take to improve boiler performance?
4. Does the vaporization of a given amount of liquid water at a given temperature require the same amount of heat transfer if the process is carried out in a closed system with reaction versus an open system with reaction?
5. Would burning a fuel with oxygen or with air yield a higher adiabatic flame temperature?
6. A recent news article said:

Two workers were killed and 45 others hurt when a blast at the _____ refinery shook a neighborhood and shot flames 500 feet into the air. Hydrogen from a "cracker unit" that separates crude oil into such products as gasoline and diesel fuel burned at temperatures from 4,000 to 5,000 degrees in the 9:50 A.M. accident at the refinery. The fire was put out about an hour later.

Is the temperature cited reasonable?

Discussion Problems

1. The Flameless Rotation Heater (FRH) was selected by *Research & Development* as one of the 100 most significant technical products of 1990. The FRH was designed for the MRE (Meal-Ready to Eat), and is considered a solution to the Armed Forces' "cold ration problem." The FRH is a 40/60 mixture of magnesium-iron powder and inert plastic powders. These materials are molded into a pad that is stable and weighs less than an ounce. The FRH comes in a bag that will also hold an MRE entrée.

A soldier in the field simply pops the 8-oz entrée into the FRH bag with a little water. The resulting exothermic reaction can raise the temperature of the entrée 100°F

in about 12 minutes. The FRH is flameless, produces no noxious combustion products, and can be activated in shelters or even in the pocket of a soldier on the move. How practical do you think the FRH is for the indicated purpose. Is the temperature cited correct?

2. An article by Joan Ogden entitled, "Hydrogen: the Fuel of the Future?" appeared in *Physics Today*, April, 2002, page 69, about energy issues for vehicles. Two of the letters to the editor that subsequently appeared (*Physics Today*, November, 2002, page 12) in reference to the article are reproduced below. Do you concur with the ideas expressed in the letters? Is a hydrogen fueled economy preferred over a conventional economy that involves the direct use of fossil fuels?

Letter No. 1

The centerpiece of the present US Department of Energy plan to improve vehicle technology apparently involves a fuel-cell-powered vehicle, the "Freedom Car." That vehicle, which would use stored hydrogen as fuel, could ultimately reduce petroleum consumption, greenhouse gas generation, and air pollution. However, a practical, economical hydrogen source that does not generate carbon dioxide will be required to obtain those benefits. The development of such a hydrogen source is a major challenge, as are the needs for practical hydrogen distribution and storage and for fuel-cell technology. It is uncertain just when such a hydrogen-powered vehicle could have a significant effect on the total fuel consumption of the US vehicle fleet; at best, that time is several decades away.

Another R&D path is likely to provide significant benefits far sooner: improving mainstream propulsion system technologies. That option would involve not only the diesel and hybrid vehicle technologies, but also much more aggressive government support for the development of high-efficiency gasoline engines. Gasoline engines currently dominate the US light-duty vehicle fleet, and their improvement should be a matter of urgency. Substantial fuel-consumption improvements, whose fuel cost savings could largely and relatively quickly offset the increase in cost, would facilitate widespread implementation, leading to significant impacts on national petroleum consumption, greenhouse-gas emissions, and reduced air pollution.

A number of new gasoline engine systems could provide significant increases in efficiency at relatively modest cost. Some of these systems may also reduce the already low emissions from gasoline-engine vehicles. Opportunities include direct fuel injection and other lean burn concepts such as hydrogen-enhanced combustion and boost, variable valve control, and variable compression ratio. Moreover, new diesel engine systems, such as boosted advanced diesels with effective exhaust trap and catalyst systems, could significantly reduce the emissions that have inhibited use of more efficient light-duty diesel vehicles. In addition, homogeneous charge compression ignition, a new low-emission, high-efficiency engine combustion concept, has potential in both diesel and gasoline engines.

Although industry does invest in developing new and improved engine technologies once their production viability is evident, many promising opportunities need substantial additional research to demonstrate that viability. The realization of those opportunities depends on the ideas and efforts of the research community, which, in turn, needs DOE support.

Increasing use of efficient low-emission diesel engines (some 30% more efficient than today's gasoline engines), coupled with widespread use of advanced gasoline engines up to 25% more efficient than today's engines, would significantly reduce US petroleum consumption. Our government's investment in R&D on these mainstream engine technology improvements is insufficient. We are especially neglecting high-efficiency gasoline engines. Because petroleum provides both gasoline and diesel fuel in comparable quantities, we need better gasoline engines, too.

Letter No. 2

The article does not explain exactly why a hydrogen economy should be preferred over the conventional economy based on direct use of fossil fuels. The article suggests that, because nuclear power and renewable energy sources (hydropower, solar, and wind) are not expected to expand enough to support the electrolysis of seawater globally, the only realistic source for hydrogen fuel is through the reforming of petroleum or natural gas.

The process of extracting hydrogen from fossil hydrocarbons—using very hot steam, for example—will produce as much carbon dioxide as if the fuel had been burned conventionally. If that CO_2 is not sequestered by some means, preferably near the hydrogen plant, its release into the atmosphere will cause as much global warming as if it had come from a conventional car or thermal power plant.

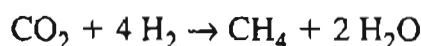
Hydrogen fuel cells do have an advantage over fossil fuels in that they produce no nitrogen oxides or particulate pollution, but improvements to conventional combustion technology have already eliminated those pollutants to a large extent. Seemingly, then, the only reason to switch to a hydrogen-based economy would be the superior energy efficiency of fuel cells, although it is not clear how much savings will remain after inefficiencies in the reforming process are factored in.

Perhaps the global environment would be better served if we tackle a much simpler problem—extending carbon sequestration technologies, already under development for large thermal plants, down to the scale of the smallest combustion engines. We could then continue with the current infrastructure for fossil-fuel distribution and use, while avoiding the complications of producing, distributing, and storing a radically new fuel.

3. A plant operator was injured when a flexible hose line ruptured when he started to transfer thionyl chloride (SOCl_2) by vacuum from a 55 gal drum. He made sure the hose was clean before starting the process by washing it with water and draining the hose thoroughly.

You are asked to investigate this accident, report on the cause(s), and recommend steps to take to prevent reoccurrence. Prepare such a report.

4. One suggestion to reduce CO_2 discharges from power plants is to convert the CO_2 into CH_4 using a rhodium-manganese catalyst at 300°C and 1 atm by the reaction with H_2 :



with 90% conversion. The CH_4 can be recycled as a fuel. How feasible is the proposed process?

5. What are some of the ways to recover waste heat from a boiler, and how can the recovered energy be used?

Looking Back

In this chapter we augmented the degree-of-freedom analysis to include the energy balance, and then proceeded to present four examples of steady flow processes in which both material and energy balances are important.

GLOSSARY OF NEW WORDS

Adiabatic reaction temperature The temperature reached when a reaction occurs in an adiabatic process with complete conversion of the limiting reactant (ignoring the effect of equilibrium).

Combustion temperature See Adiabatic reaction temperature.

Flame temperature See Adiabatic reaction temperature.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

Degrees of Freedom

Dixon, D. C. "Degrees of Freedom in Dynamic and Static Systems," *Ind. Eng. Chem. Fund.*, **11**, 198–205 (1972).

Kwauk, M. "A System for Counting Variables in Separation Processes," *A.I.Ch.E.J.*, **2**, 240–248 (1956).

Luyben, W. L. "Design and Control Degrees of Freedom," *Ind. Eng. Chem. Res.*, **35**, 2204–2214 (1996).

Morse, P. L. "Degrees of Freedom for Steady State Flow," *Ind. Eng. Chem.*, **43**, 1863–1871 (1951).

Reklaitis, G. V. *Introduction to Material and Energy Balance*, John Wiley, New York (1983).

Suggested Reading

Alcock, C. B. *Thermochemical Processes: Principles and Models*, Butterworth-Heinemann, Woburn, MA (2001).

Black, W. Z. and J. G. Hartley. *Thermodynamics*, Harper & Row, New York (1985).

Glassman, I. *Combustion*, Academic Press, New York (1977).

Hanby, V. I. *Combustion and Pollution Control in Heating Systems*, Springer Verlag, London (1994).

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Tomeczek, J. *Coal Combustion*, Krieger, Melbourne, FL (1992).

Van Wylen, G. J., and R. E. Sonntag. *Fundamentals of Classical Thermodynamics*, 3rd ed. New York (1986).

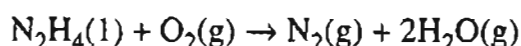
Web Sites

www.fuelcelltoday.com

<http://voyager5.sdsu.edu/testcenter/features/ossteady/index.html>

PROBLEMS

- *26.1 Can savings in energy be achieved by shutting down heating equipment when it is not in use in off-hours rather than leaving the equipment on all the time? For example, an oil burning furnace is used to reheat steel to 1230°C and requires 270L/hr of fuel oil on idle to maintain this temperature. If cooled to ambient temperature the furnace can be reheated in 6.5 hours while burning fuel oil at the average rate of 760L/hr. How much money can be saved by shutting the furnace down each weekend if fuel oil is \$0.19/L? What problems might occur with the proposed procedure? *Data:* The heat of reaction at the furnace operating temperature is 40,000 MJ/L of fuel oil.
- *26.2 Does the presence of N₂ in the air affect the outcome of a combustion process? How?
- *26.3 Does the presence of moisture in the air affect the outcome of a combustion process? How?
- *26.4 Complete the following sentences in the blank spaces provide with either the word increases or decreases:
- For a fixed outlet flue gas temperature from a heater, increasing the excess air _____ the outlet flue gas temperature.
 - For a fixed outlet flue gas temperature, increasing the inlet air temperature _____ the thermal efficiency of the heater.
 - For a fixed amount of excess air, increasing the return of flue gas to preheat the entering air _____ the fuel consumption for a fixed load on the heater.
- 26.5 Liquid hydrazine (N₂H₄) is injected into a jet combustion chamber at 100°C, where it is ignited and burns in an air stream with 100% excess air preheated to 500°C. The hot gases issue directly from the end of the reactor. What is their temperature?



In the standard thermochemical state:

N ₂ H ₄ (g): ΔH_c (gross)	-45.570 kg cal/g mol
N ₂ H ₄ (l): molal ΔH_{vap}	10.7 kg cal/g mol
molal heat capacity, a constant	33.2 cal/(g mol)(°C)
H ₂ O (l) molal ΔH_{vap}	10.8 kg cal/g mol

Enthalpies of gases in cal/g mol:

T(°C)	N ₂	O ₂	H ₂ O
0	0	0	0
25	174	175	200
100	696	706	806
500	3,570	3,745	4,254
1000	7,482	7,916	9,210
1500	11,650	12,290	14,790
2000	15,970	16,810	20,800
2500	20,340	21,470	27,090
3000	24,770	26,250	33,540

If you use data from the CD you do not have to use the data listed above.

- **26.6** Many families heat their homes with butane (C_4H_{10}). If the furnace uses $20 \text{ ft}^3/\text{min}$ of butane at 15.5 psia and 70°F in the burner together with 20% excess air, how many ft^3/min of product gases at 900°F and 14.9 psia go into the heat exchanger that is placed after the burner. (The house air and the product gases do not mix; they are separated by the heat exchanger walls.) If the air enters at 77°F , what is the enthalpy change that occurs in the furnace?
- *26.7** Fluidized beds (see Figure P26.7) are used in the chemical industry as steam generators. Such equipment can burn almost any fuel, including low-quality coals such as lignite.

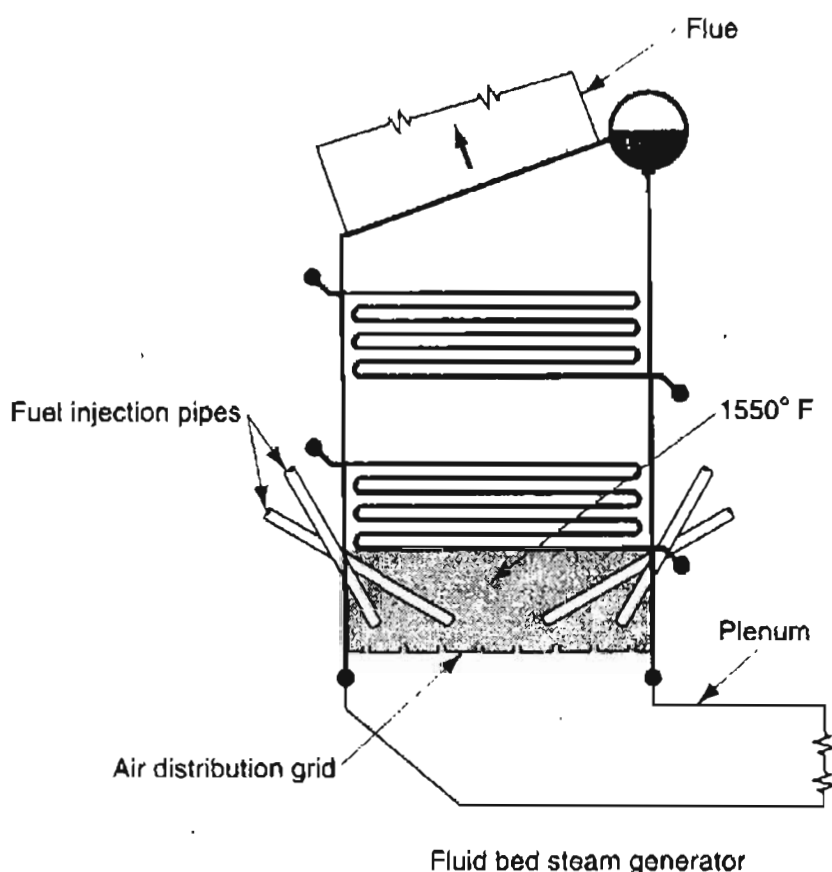


Figure E26.7

Coal burns rapidly in a fluidized bed, even at 1500°F . Based on bed volume, the heat release is $300,000\text{--}400,000 \text{ Btu}/(\text{hr})(\text{ft}^3)$. Counting the open furnace space above the bed the rate is $100,000\text{--}200,000 \text{ Btu}/(\text{hr})(\text{ft}^3)$.

Suppose that $200,000 \text{ Btu}/(\text{hr})(\text{ft}^3)$ are generated in a 40 ft^3 steam generator, that the water enters the two sets of coils at 70°F , and that in the upper set of coils the water flow rate is $3,000 \text{ lb/hr}$ leaving as steam at 900°F and 380 psia . If the steam leaving the lower coils is at 1200°F and 400 psia , what is the flow rate of the water into the lower set of coils?

- *26.8** The energy of gases that are exhausted to the atmosphere is really energy that has been paid for and should not be wasted. With some modest capital expenditure, waste

heat recovery units such as heat exchangers can be added to a process unit economically, and achieve considerable monetary savings. The heat recovered from the heat exchanger can be used to preheat combustion air, preheat boiler feedwater, provide domestic hot water, and so on.

In Problem 25.7, suppose that 1.3×10^4 ft³/hr of flue gas of composition 13.4% CO₂, 3.6% O₂, and 83.0% N₂ exit at 950°F and 1 atm. You are asked to design a waste heat recovery heat exchanger that exchanges heat with air that enters at 77°F and exits at 300°F. Allow for a temperature difference between the flue gas and the air so that the flue gas exits at 350°F. (The flue gas and air do not mix.) To size the exchanger you are asked to calculate the ft³ of air that will flow through the exchanger per hour. Suggestion: Use the physical property software on the CD that accompanies this book to make the calculations simple.

- *26.9** One of the proposed ways to obtain higher efficiency from fuels in vehicles and avoid pollutants (and carbon dioxide) is by the use of fuel cells. A fuel cell is an electrochemical device operating continuously that uses fuel and oxygen (or another reactant) to produce electricity. Fuel is oxidized at the anode, giving up electrons to an external circuit where they are transported to the oxidant that takes up the electrons and is reduced at the cathode. Look at Figure P26.9 that shows the oxidation of hydrogen in an alkaline (KOH) electrolyte.

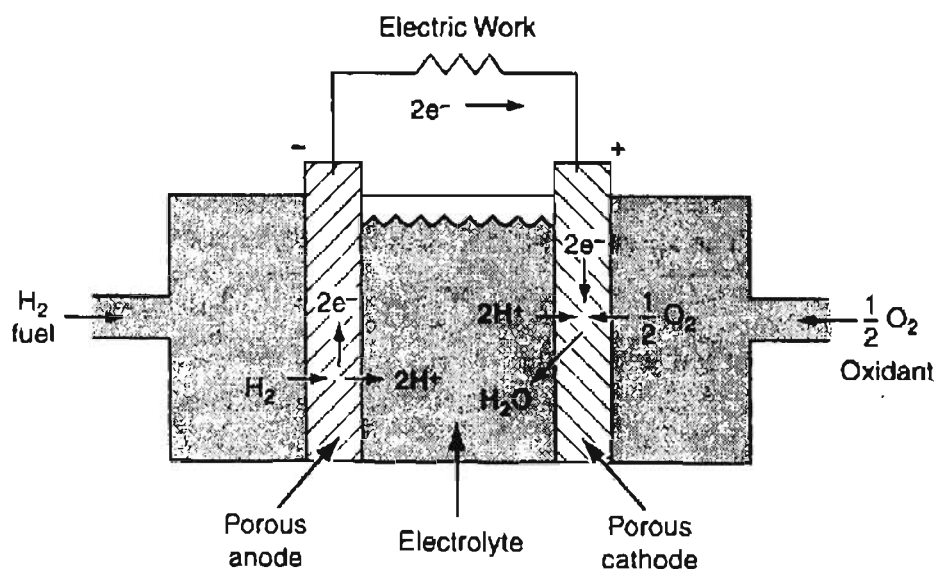


Figure E26.9

If the hydrogen is reacted with the stoichiometric amount of oxygen as indicated in Figure P26.9, and the fraction conversion of the hydrogen is 0.65 in an insulated cell, how many kWh can be obtained from the cell at 85°C per gram mole of hydrogen fed to the cell?

- **26.10** Various alternative fuels have been proposed to replace gasoline. Prepare a table that list the following fuels:
- (1) Iso-octane (C₈H₁₈)
 - (2) Ethyl alcohol (C₂H₅OH)

(3) Methyl alcohol (CH_3OH)

(4) Compressed natural gas (CNG) (say CH_4)

along with the following in succeeding columns:

(1) Pounds per gallon

(2) Heat of combustion in Btu/lb mol

(3) Heat of combustion in Btu/gal

(4) Miles per gallon relative to iso-octane which you can assume gets 40 miles per gallon. Let iso-octane be at the top of the scale with a value of 100.

(5) Based on (4) list the miles per gallon expected.

(6) Gallons consumed per 1000 miles traveled.

(7) Pounds of CO_2 emitted per gallon.

(8) Based on (7) list the percent CO_2 more or less than iso-octane.

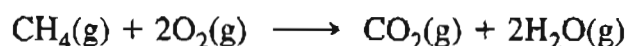
(9) Pounds of CO_2 emitted per 1000 miles traveled.

****26.11** Several nearby businesses are complaining that the exhaust air from a barbecue store stinks. To eliminate the obnoxious fumes and odors the owner plans to incinerate his 5000 ft^3 per minute exhaust fan discharge (which is at 130°F and 1 atm) with natural gas (methane) which has a HHV of 1059 Btu/ ft^3 . Ignore any heat losses, and calculate the ft^3 per minute of natural gas required to raise the new exhaust gas temperature up to 1200°F , the temperature needed to eliminate the odors.

****26.12** Calculate the adiabatic flame temperature of $\text{C}_3\text{H}_6(\text{g})$ at 1 atm when burned with 20% excess air, and the reactants enter at 25°C .

***26.13** Which substance will give the higher theoretical flame temperature if the inlet percentage of excess air and temperature conditions are identical: (a) CH_4 , (b) C_2H_6 , or (c) C_4H_8 ?

****26.14** Calculate the adiabatic flame temperature of $\text{CH}_4(\text{g})$ at 1 atm when burned with 10% excess air. The air enters at 25°C and the CH_4 at 300K. The reaction is



****26.15** A gas is burned with 300% excess air with the gas and air entering the combustion chamber at 25°C . What is the theoretical adiabatic flame temperature achieved in $^\circ\text{C}$? See Figure P26.15.

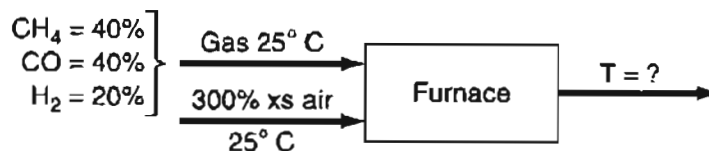


Figure P26.15

***26.16** A gaseous fuel of 50% CH_4 and 50% N_2 at 100°F and 1 atm burns with 20% excess air supplied at 60°F and 1 atm. Suggest three different ways to increase the adiabatic reaction temperature of the process. No numerical calculations are needed, but explain (justify) your recommendations in detail.

****26.17** If CO at constant pressure was burned with excess air and the measured temperature of the exit gases was 981°C. What was the percentage of excess air used? The reactants entered at 93°C.

*****26.18** Three fuels are being considered as a heat source for a metallurgical process:

	Components	Percent
Gas	CH ₄	96.0
	CO ₂	3.0
	N ₂	1.0
Oil (liquid)	C ₁₆ H ₃₄	99.0
	S	1.0
Coke	C	95.0
	ash	5.0

Calculate the maximum flame temperature (i.e., combustion with the theoretically required amount of air) for each of the three fuels assuming that the fuels and air enter at 18°C, and the ash ($C_p = 1.15 \text{ J/(g)(°C)}$) leaves the combustion chamber containing no carbon and at 527°C. Which fuel gives the highest temperature?

****26.19** An old idea now coming into vogue for efficient heat transfer is to operate a submerged combustion burner (see Figure P26.19) to give hot water. The fuel, natural gas, may be assumed to be CH₄ and is burned using 5% excess air. The immersion of the burner is such that the flue gases leave the water in equilibrium with it. The feedwater enters the dehumidifier section at 190°F and the hot water leaves from the bottom of the combustion chamber at 310°F. The CH₄ and air enter dry at 60°F. Calcul-

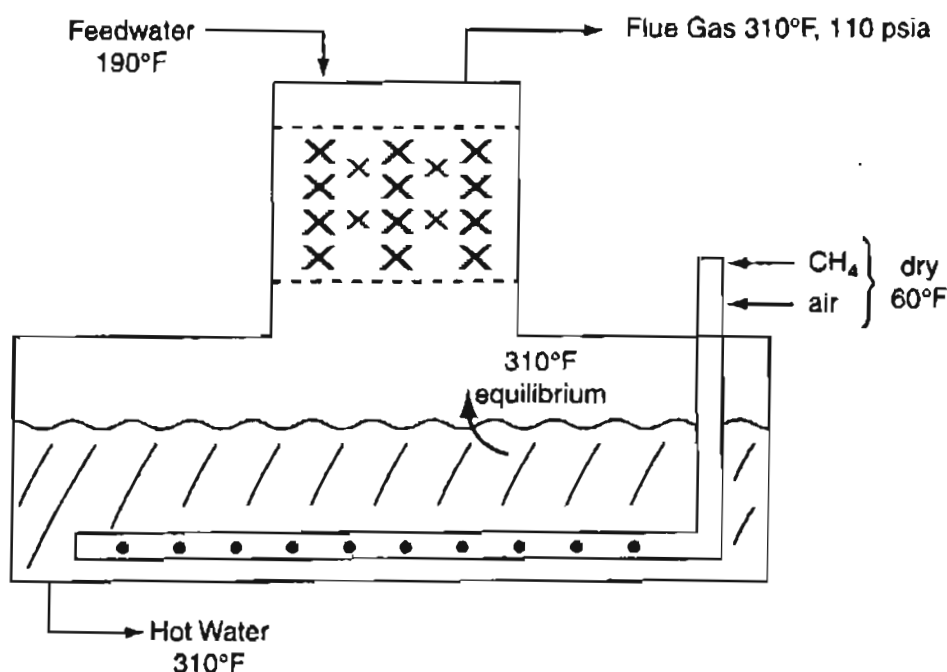


Figure P26.19

late the lb of 310°F water provided per lb of CH_4 burned. Assume that the flue gas leaving the vessel is at 310°F and 110 psia in equilibrium with the hot water, and that the tank is insulated.

- **26.20** Constant-volume vessels that contain flammable mixtures of hydrogen and air are frequently used. Although the ignition of such mixtures is very unlikely as there is no source of ignition in the tank, the Safety and Design Codes require that the tank withstand four times the pressure that may occur should an explosion take place in the tank.

A fixed volume tank contains a mixture of 1 g mol of hydrogen (H_2) gas and the stoichiometric amount of air at 25°C and 1 atm. The contents of the tank are now ignited. Assuming complete combustion, determine the final temperature in the tank immediately after the explosion (reaction), and decide if the final pressure exceeds the pressure limits for the tank (4000 kPa).

- **26.21** A flexible vessel maintains a constant pressure of 300 kPa during a combustion process. The vessel has an initial volume of 0.8 m³ and contains a stoichiometric mixture of octane (C_8H_{18}) gas and air at 25°C. The mixture is ignited, and the product gases are observed to be at 1000 K at the end of the combustion process. Assume complete combustion occurs and that the reactants and the products are ideal gases. Determine the heat transfer from the vessel during the process.

- **26.22** The Neches Butane Products Co. makes butadiene, C_4H_6 , by separating butenes, C_4H_8 , from refinery gases piped to them, and then further dehydrogenating the butenes to butadiene. In order to increase capacity they would like to be able to dehydrogenate butane, C_4H_{10} , in one step without the intermediate separation of the butene. The C_4H_6 formed would be separated, and any unreacted C_4H_{10} or C_4H_8 would be recycled to the reactor. One of the large engineering companies claims to have such a process. You have just been employed by Neches B.P. Co.—fresh from school—and are requested to make some calculations on the proposed process:



By heat exchange, the butane fed into the reactor is brought to the reaction temperature of 1000 K. It is desired to maintain an isothermal reactor. How much heat must be added or removed per g mole of butadiene formed? Assume the pressure is 100 kPa. What are some reasons why the heat load may be different from the value you calculate?

- **26.23** Formaldehyde can be made by the oxidation of methanol (CH_3OH). If stoichiometric amounts of $\text{CH}_3\text{OH}(\text{g})$ and $\text{O}_2(\text{g})$ enter the reactor at 100°C, the reaction is complete, and the products leave the reactor at 200°C, calculate the heat that is added or removed from the reactor per mole of $\text{CH}_3\text{OH}(\text{g})$ fed to the reactor. The reaction is



- ***26.24** Liquid hydrazine (N_2H_4) is injected in a jet combustion chamber at 400 K and burned with 100% excess air that enters at 700 K. The combustion chamber is jacketed with water. The combustion products leave the jet exhaust at 900 K. In the test, if 50 kg

mol of N_2H_4 are burned per hour and water at 25°C enters the water jacket for cooling at the rate of 400 kg/min, what volumetric flow rate of the water (liquid plus vapor) will the exit line for the water have to accommodate (at 1 atm)? The reaction is



Data:

$$\Delta \hat{H}_f^\circ \text{ of } \text{N}_2\text{H}_4(\text{l}) = 44.77 \text{ kJ/g mol} \quad C_p \text{ of } \text{N}_2\text{H}_4(\text{l}) \approx 139 \text{ J/(g mol)}(^\circ\text{C})$$

- ***26.25 A flue gas analysis was run on a natural gas (CH_4) fired boiler, and showed 7.8% CO_2 and 3.9% O_2 with the flue gas exiting the boiler at 515°F . By reducing the excess air until the flue gas showed 8.7% CO_2 and 1.9% O_2 , the exit temperature of the flue gas was reduced to 490°F for the same heat duty (Q).

To maintain these latter operating conditions, it was proposed to install a control system that cost \$31,000 installed. If the natural gas cost $\$1.55/10^6$ Btu, and the process used $180,000 \text{ ft}^3/\text{hr}$ of gas (at SC), with 8000 hours of operation per year, how long would it take to save \$31,000 in fuel costs if operations were carried out at the second set of conditions?

- **26.26 An engine that is used to drive a compressor discharges $4225 \text{ ft}^3/\text{min}$ of exhaust at 1100°F and 6 inches of water back pressure. The plant requires 2000 lb/hr of 15 psig steam, which was supplied by a fired boiler using #2 fuel oil (density = 7.2 lb/gal , LHV = $18,300 \text{ Btu/lb}$), and has available 220°F water for boiler feedwater. Calculate the exhaust heat recovered by a waste heat recovery muffler in lb/hr of steam (thus allowing the output of steam from the fired boiler to be reduced resulting in the substantial fuel oil savings). Assume 80% efficiency in the boiler. Calculate the annual fuel savings based on 4500 hours of operation per year in Btu/yr , gallons of oil per year, and dollar savings if oil is $\$0.50/\text{gal}$.

- **26.27 Although processes are designed to avoid releases of flammable and toxic substances into the surroundings, accidents do happen. Consequently, it is best to evaluate during the design phase the consequences of a hypothesized spill or leak so that emergency actions can be taken to mitigate the consequences of the accident. For liquid releases, the amount of vapor formed is critical, particularly for flammable vapors as the vapor can be blown by the wind beyond the site of the accident.

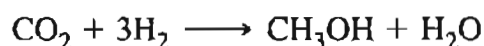
In a process under consideration, two possible liquid solvents are being considered: methanol and n -heptane. If an accident occurs, estimate the amount of vapor that would be generated for each solvent if it took 10 minutes before the flow of solvent could be shut off. Also estimate the total energy released if the vapor cloud burned completely. You want to choose the solvent that (a) generates the smallest vapor cloud, and (b) releases the least energy on combustion.

Process information: The normal solvent flow at some points in the process will be 500 gal/min , but the estimated flow through a broken pipe will be double the normal rate. The liquid temperature in the flowing stream will be as high as 400°F . The lower flammability limits are: CH_3OH (6.7%) and $n\text{-C}_7\text{H}_{16}$ (1.05%).

Hints: To help in the choice of which solvent to use, first estimate the fraction of the liquid that will vaporize under three assumed conditions: (a) The liquid and vapor are at the normal boiling point following the release, (b) the liquid and vapor cool to an ambient temperature of 80°F following the release, and (c) the liquid and vapor cool to 25°F following the release. The last estimate is based on an analysis of heat transfer between the liquid-vapor mixture and the surrounding air. Get the enthalpy data for each solvent from a handbook or a computer database. Assume the vapor mixes with the air. Then determine the vapor cloud size based on having a mixture at its lower flammable limit, and assume the mixtures of vapor and air will be ideal because the mixture will be at a low pressure. Finally, calculate the energy released on combustion of the vapor release.

Adapted from Problem 48 in *Safety, Health, and Loss Prevention in Chemical Processes*. New York: American Institute of Chemical Engineers, 1990.

- ***26.28 A proposed method of producing methanol (that might be used as an alternate fuel) is to react CO_2 with H_2 (Figure P26.28)



Assume that the gross feed enters the reactor in the stoichiometric quantities needed for the reaction. Also 0.5% N_2 flows in with the fresh feed. On one pass through the reactor 57% conversion is obtained. The concentration of N_2 in the gross feed into the reactor cannot exceed 2%.

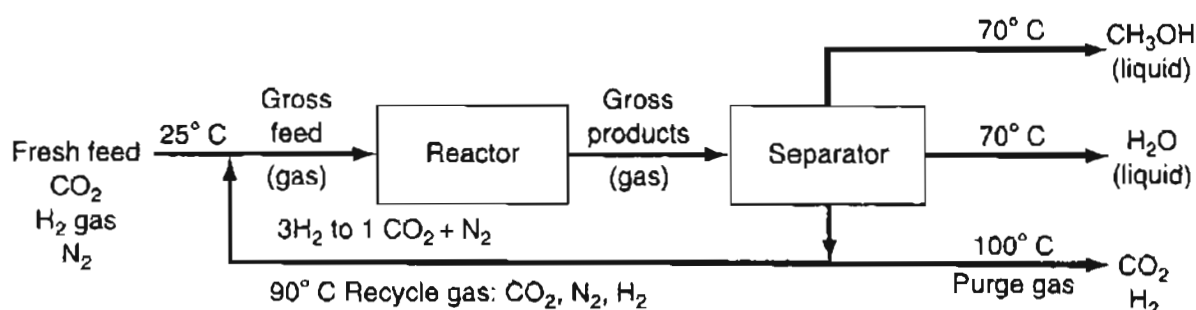
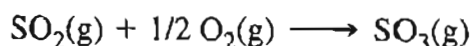


Figure E26.28

Assume the process is in the steady state, that all gases are ideal, and the reaction system is as shown in the accompanying figure. How much heat must be added or removed from the entire system? The heat capacity of liquid CH_3OH from Perry in the range of 0 to 98°C is 0.68 cal/(g)(°C).

- ***26.29 Sulfuric acid is a major bulk chemical used in a wide variety of industries. After sulfur is oxidized to SO_2 , the SO_2 is further oxidized in the converters (reactors) to SO_3



and the SO_3 is absorbed in dilute H_2SO_4 to form concentrated H_2SO_4 .

In the first converter the entering gases at 400 K and 1 atm are composed of 9.0% SO_2 , 9.5% O_2 , and 81.50% N_2 . Only 75% of the entering SO_2 reacts on going

through the first converter. If the maximum temperature of the gas before going to the next converter (where the reaction is completed) can be 700 K, how much heat must be removed from the gas before it goes to the second converter per kg mol of S entering the process?

- *26.30 Cell growth liberates energy which must be removed; otherwise, the temperature will rise so much that the cells may be killed. In a continuous fermenter for the production of *Penicillium chrysogenum*, the cells generate 27.6 kJ/L per hour, and the volume of the well-insulated fermenter is 2 L. The feed temperature is 25°C and the exit temperature is equal to the temperature in the fermenter. *Penicillium chrysogenum* cannot grow above 42°C. Will the cells survive? Assume for simplicity that the inlet and outlet streams have a heat capacity of 4 J/(g)(°C) and the mass flow rates of 1025 g/hr are constant.

CHAPTER 27

IDEAL PROCESSES, EFFICIENCY, AND THE MECHANICAL ENERGY BALANCE

27.1 Ideal Reversible Processes

837

27.2 Efficiency

843

27.3 The Mechanical Energy Balance

848

Your objectives in studying this chapter are to be able to:

1. Explain what a reversible process is.
2. Identify a process as reversible or irreversible given a description of the process.
3. Define efficiency and apply the concept to calculate the work for an irreversible process.
4. Write down each of the terms in the steady-state mechanical energy balance for an open system, and understand the conditions under which the equation can be applied.
5. Apply the mechanical energy balance when appropriate to problems so that you can predict pressure drops, velocities, friction losses, and pump sizes.

The ideal process is a hypothetical process that rarely occurs in practice. Why bother with it then? The reason is that calculations for energy changes can be made for an ideal process, and then an empirical *efficiency* used to convert the ideal work or energy change into the actual work or energy change. Understanding how non-ideal (real) processes degrade the usefulness of various kinds of energy will help you avoid investing in perpetual motion machines.

Looking Ahead

In this chapter we examine certain types of ideal processes called reversible processes. Then we go on to discuss various kinds of efficiencies. Finally, we describe and apply to practical problems a type of energy balance called the mechanical energy balance.

27.1 Ideal Reversible Processes

If you can keep your head when all about you are losing theirs, maybe you just don't fully understand the situation.

Sign in a Pentagon office

The critical issue in designing and operating processes is not the conservation of energy, for example, applying the general energy balance. Energy in the system plus the surroundings (the **universe**) is *always* conserved. What is of concern is how energy can be converted from one form to another, and how efficiently the conversion can be made to take place. To characterize the interactions of energy within a system, and between the system and its surroundings, as the system moves from one state of equilibrium to another, scientists pose two types of processes:

1. **Reversible:** an idealized process (primarily hypothetical) in which changes occur because of an infinitesimal (differential) imbalance of temperature, pressure, and so on.
2. **Irreversible:** a process that is not reversible because it occurs with finite differences of temperature, pressure, etc.—most real processes.

As you might infer from the name, a reversible process is one in which the states of the system plus the surroundings can be reversed by a differential change in the driving potential (dT , dp , etc.). What we do is to characterize a process in words as “a controlled, very slow expansion,” “frictionless,” “elastic spring,” and so on, so that it can be treated as reversible in your calculations. Examine Figure 27.1.

Example 21.1 in Section 21.1 illustrated the calculation of reversible work. Note that the piston in Figure 27.1 moves downward so that the potential energy of the center of mass of the gas changes slightly on expansion.

Irreversible processes involve dissipative effects and nonequilibrium transfers of energy. Both types of processes increase molecular disorder. Examples are the mixing of dissimilar substances, electrical resistance, sudden changes in phase, mass transport under finite concentration difference, pipe flow, and so on. In Figure 27.1b, what happens to the work being done by the gas on the piston during the ex-

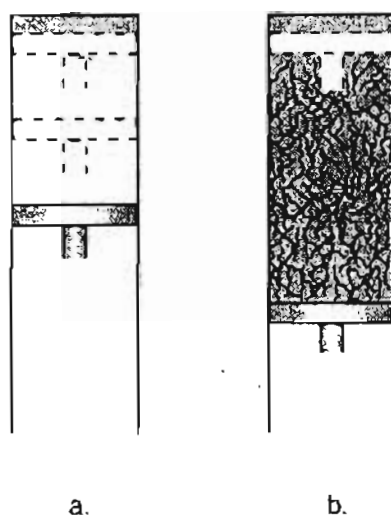


Figure 27.1 Comparison of two hypothetical processes for a short time interval. Figure 27.1a compares a reversible process with an irreversible process shown in Figure 27.1b: (a) is a very slow expansion of gas without friction between the piston and the chamber wall; (b) is a fast expansion of a gas with friction between the piston and the wall and turbulence.

pansion of the gas if the process is irreversible? Some of the work causes the piston to go down, and thus stores the energy in a device that later on can itself do work. But some of the work is converted to thermal energy (U) in the piston, the cylinder, and the gas, energy that cannot be completely recovered as work. Thus, if the piston were returned to its original state in Figure 27.1b by doing work to compress the gas, you would find that the surroundings had to supply some extra work to complete the return to the original state.

EXAMPLE 27.1 Calculation of the Work Done during Evaporation of a Liquid

How much work is done by 1 liter of saturated liquid water when it evaporates from an open vessel into the atmosphere where the pressure is 100 kPa?

Solution

Example 27.1 illustrates one real process that is essentially reversible.

Steps 1, 2, 3, and 4

The system is the water. The process is an open system. Does the water do work in evaporating? Certainly! It does work against the atmosphere by pushing it back. Furthermore, the process diagrammed in Figure E27.1, is a reversible one because the evaporation takes place at constant temperature (372.78 K) and pressure, and presumably the conditions in the atmosphere immediately above the open portion of the vessel are in equilibrium with the water surface. The atmospheric pressure is 100 kPa. The basis will be 1 L of liquid water that vaporizes to a gas. The specific volume of the water vapor is $1.694 \text{ m}^3/\text{kg H}_2\text{O}$.

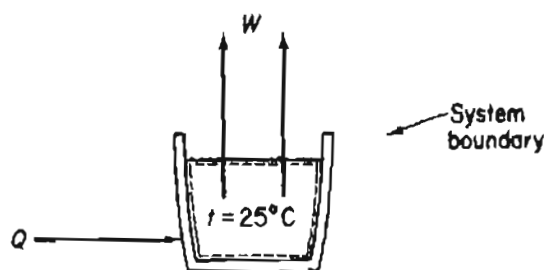


Figure E27.1

Step 5

Basis: 1 L of water (liquid).

Steps 6 and 7

The unknown quantity is the work done by the liquid water pushing against the atmosphere. The general energy balance

$$\Delta E = Q + W - \Delta[(\hat{H} + \widehat{KE} + \widehat{PE})_m]$$

will not be useful in solving this problem because Q is unknown. Even though the system is actually an open one, imagine that an expandable bag is placed over the open face of the vessel so that the system comprised of the water becomes a closed system. Because of the reversible assumption established for this problem, the work for a closed system is

$$W = - \int_{V_1}^{V_2} p dV = -p\Delta V$$

which represents the reversible work done by the water filling the hypothetical bag in pushing back the atmosphere.

Steps 8 and 9

The specific volume of the liquid water from the SI stream tables is $0.001043 \text{ m}^3/\text{kg}$. The final volume of the water vapor is (the initial volume of H_2O in the bag is zero and we will assume that there is enough water in the vessel so that the loss of liquid water to vapor is negligible)

$$\frac{1 \text{ L liquid}}{1000 \text{ L}} \left| \frac{1 \text{ m}^3}{1000 \text{ L}} \right| \left| \frac{1 \text{ kg}}{0.001043 \text{ m}^3 \text{ liquid}} \right| \left| \frac{1.694 \text{ m}^3 \text{ vapor}}{\text{kg}} \right| = 1.624 \text{ m}^3 \text{ vapor}$$

$$W = - \frac{100 \times 10^3 \text{ Pa}}{1 \text{ Pa}} \left| \frac{1 \text{ (N)/(m}^2\text{)}}{1 \text{ Pa}} \right| \left| \frac{1 \text{ J}}{1 \text{ (N)(m)}} \right| \left| \frac{1.624 \text{ m}^3}{1 \text{ (N)(m)}} \right| = -1.624 \times 10^5 \text{ J}$$

EXAMPLE 27.2 Calculation of the Work in a Batch Process

One kilogram mole of N_2 gas is in a horizontal cylinder at 1000 kPa and 20°C . A 6 cm^2 piston of 2 kg mass seals the cylinder and is fixed by a pin. The pin is released, and the N_2 volume is doubled, at which time the piston is stopped again. What is the work done by the gas in this process?

Solution**Steps 1, 2, 3 and 4**

Draw a picture. See Figure E27.2. From the ideal gas law you can compute the specific volume of the gas at the initial state

$$\hat{V}_1 = \frac{RT}{p} = \frac{8.31 (\text{kPa})(\text{m}^3)}{(\text{K})(\text{kg mol})} \left| \frac{293 \text{ K}}{1000 \text{ kPa}} \right| = 2.435 \text{ m}^3/\text{kg mol}$$

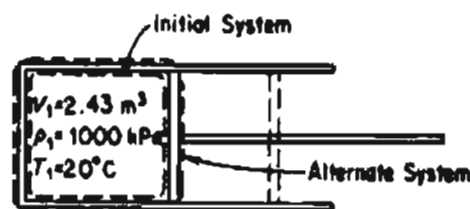


Figure E27.2

- Is the process a flow or a nonflow process? Since no material leaves or enters the cylinder, let us analyze the process as a closed system.
- This process is definitely irreversible because of friction between the piston and the walls of the cylinder, turbulence in the gas, the large pressure drops, and so on.

Choose the gas to be the system.

Step 5

We can use as a basis 2.435 m^3 of N_2 at 1000 kPa and 20°C .

Steps 6 and 7

We want to calculate the work done by the gas on the piston and the cylinder. As in Example 27.1, the work cannot be calculated from the general energy balance because Q is unknown. Furthermore, because the process is irreversible, you cannot calculate the work done on the piston by $-\int p dV$.

Let us change our system to include the gas, the piston, and the cylinder. With this choice, the system expansion is still irreversible, but the pressure in the surroundings can be assumed to be atmospheric pressure and is constant. The work done in pushing back the atmosphere probably is done almost reversibly from the

viewpoint of the surroundings, as assumed in Example 27.1, and can be closely estimated by calculating the work done by the alternate system on the surroundings.

$$W = - \int_{V_1}^{V_2} p \, dV = -p \Delta V$$

ΔV of the gas is $2V_1 - V_1 = V_1 = 2.435 \text{ m}^3$, so that the volume change of surroundings is -2.435 m^3 . Then the work done on the surroundings is

Basis: 2.435 m^3 at 101.3 kPa and 20°C (assumed)

$$W = - \frac{101.3 \times 10^3 \text{ Pa}}{1} \left| \frac{-2.435 \text{ m}^3}{1 \text{ Pa}} \right| \left| \frac{1(\text{N})(\text{m}^{-2})}{1 \text{ Pa}} \right| \left| \frac{1 \text{ J}}{1(\text{N})(\text{m})} \right| = 247 \text{ kJ}$$

From this we know that the work done by the alternate system is

$$W_{\text{system}} = -W_{\text{surroundings}} = -247 \text{ kJ}$$

This answer still does not answer the original question of what work was done by the gas, because the revised system now includes both the piston and the cylinder as well as the gas. You should also note that if the surroundings were a vacuum instead of air, then *no work* would be done by the system consisting of the piston plus the cylinder plus the gas, although the gas itself probably still would do some work on the piston.

How would the above calculation be changed if the piston/cylinder/gas equipment were vertical rather than horizontal? Hint: Think about potential energy.

SELF-ASSESSMENT TEST

Questions

1. The following statement appeared in a text:

"The work performed for any gas process is represented by the area under a pressure-volume diagram and may be found by the following expression."

$$W = \int p \, dV$$

Comment on this statement.

2. An ideal gas produces 475 J of work in a reversible expansion in an isothermal process; $p_1 = 1 \text{ atm}$ and $p_2 = 0.1 \text{ atm}$. You are asked to calculate Q , ΔH , and ΔE for this expansion. Can you do so?
3. Can you apply $\int p \, dV$ to calculate work in a batch reversible process for which the system is a liquid? A solid?

- Which process will yield more work: (1) expansion of a gas confined by a piston against constant pressure, or (2) reversible expansion of a gas confined by a piston?
- Define a reversible process.

Problems

- Find Q , W , ΔE , and ΔH for the reversible compression of 3 moles of an ideal gas from a volume of 100 dm^3 to 2.4 dm^3 at a constant temperature of 300 K .
- You let 1 mole of an ideal gas expand against an external pressure of 1.12 atm . The initial volume of the gas is 23.17 dm^3 , and the final volume is 35.22 dm^3 . What is the work done on the system in this process? (Assume $p_{\text{sys}} = p_{\text{sur}}$ at the end of the process, and that T is constant.) Then you carry out by some means a reversible isothermal expansion of the same ideal gas. Will the work be larger or smaller in the second case? Calculate it.

Thought Problem

- Look at Figure 27.1TP1. This apparatus appeared in a magazine with the statement that once the funnel was filled, it ran continuously for 12 hours before stopping. Do you believe it?

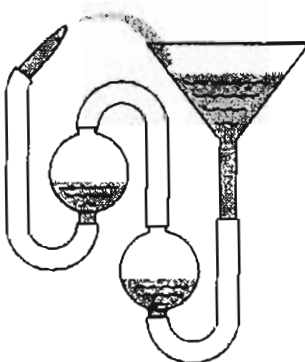


Figure 27.1TP1

Discussion Problem

- Discuss the feasibility of the following novel proposal as a way to extract energy from river flow that would not require large dams. See Figure DP27.1P1. The apparatus consists of a pair of tall chambers connected at the top by a tube containing an air turbine the diameter of a dinner plate. As the water flows through the system, one chamber fills, pushing air past one side of the turbine; the other side empties, sucking air from the tube.

Whereas a standard turbine uses a conventional fan blade that spins according to the direction of the water, the counter-rotating turbine in the proposed system uses a blade shaped like an airplane wing that creates lift to spin the turbine when the airflow rushes over its front edge. The blades are placed around the turbine in paddlewheel fashion. As the first water chamber fills, air whooshes through the tube and hits the front of the paddlewheel, lifting each blade upward as it spins past the airflow. As the first chamber emp-

ties and the other fills, air races in the opposite direction through the tube and over the blades at the rear of the paddlewheel. The blades, having spun halfway around the wheel, are now upside down, so the “lift” pulls them downward. Thus, even though the airflow reverses with each cycle, the turbine rotates in the same direction, generating a constant flow of electricity.

Simple gates and counterbalances at the bottom coordinate the operation of the unit as the chambers alternately fill and empty. At the top of the cycle, water pressure inside the filled chamber exceeds the pressure exerted by a counterweight on the outflow door at the bottom of the chamber, popping it open. The same motion closes the outflow gate in the opposite chamber, thanks to a single shaft that controls the two gates

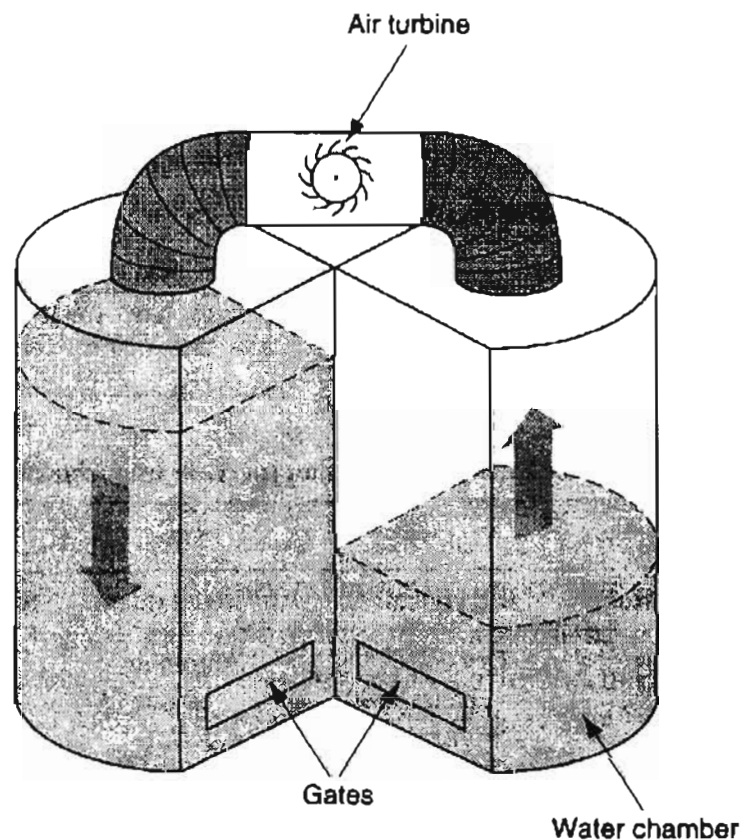


Figure DP27.1P1

27.2 Efficiency

If you look in the dictionary for the meaning of the word **efficiency**, you find: “the ratio of the work done by an organism or machine to the amount of food or fuel consumed and to the energy expended.” In engineering you will encounter a variety of more precise definitions of efficiency, some of which are listed in Table 27.1. Numerous other specialized quantities termed efficiencies exist for hydroelectric plants, other power plants, automobile engines, transmissions and drive trains, furnaces, combustion processes, and so on. Table 27.2 lists some typical values of efficiencies of common equipment.

TABLE 27.1 Various Process Efficiencies

General efficiency

$$\eta_1 = \frac{\text{useful energy out}}{\text{energy in}}$$

Mechanical efficiency

$$\eta_2 = \frac{\text{actual work output from the process}}{\text{work output for a reversible process}}$$

$$\eta_3 = \frac{\text{work input for a reversible process}}{\text{actual work input for the process}}$$

Heat engine efficiency

$$\eta_4 = \frac{\text{actual work output from the process}}{\text{heat input from a source}}$$

Refrigeration cycle efficiency

$$\text{Coefficient of performance: COP} = \frac{\text{heat removed from process}}{\text{work input to the process}}$$

TABLE 27.2 Efficiencies of Energy Conversion (percent in parenthesis)

FROM	TO				
	Chemical	Electrical	Mechanical	Radiant	Thermal
Chemical		Dry cell battery (90) Storage battery (70) Fuel cell (60) Gas turbine (30)	Automobile engine (37) Aircraft engine (37)		Boilers (88) Home gas furnace (85) Home oil furnace (65) Steam power plant (40) Steam turbine (45)
Electrical	Storage battery (70)			Flourescent tube (25) Incadescent bulb (5)	
Mechanical		Electric generator (98)			
Radiant		Solar cell (10)			
Thermal		Thermocouple (8)			

EXAMPLE 27.3 Efficiency of Power Generation by a Hydroelectric Plant

A small hydroelectric plant puts out 20 MW when the level of water above the generators is 25 m and the water flow rate through the generators is 100 m³/s. What is the overall efficiency of the plant?

Solution

The mass flow rate of the water (density 1000 kg/m³) is

$$\frac{100 \text{ m}^3}{\text{s}} \left| \frac{1,000 \text{ kg}}{\text{m}^3} \right| = 10^5 \text{ kg/s}$$

The potential energy change of the water per second is

$$\Delta \dot{P}E = \dot{m}gh = \frac{10^5 \text{ kg}}{\text{s}} \left| \frac{9.807 \text{ m}}{\text{s}^2} \right| \left| \frac{25 \text{ m}}{\text{m}} \right| \left| \frac{(\text{s}^2)(\text{J})}{1(\text{kg})(\text{m})} \right| \left| \frac{(\text{s})(\text{W})}{1 \text{ J}} \right| = 2.45 \times 10^7 \text{ W}$$

$$\eta = \frac{20 \times 10^6 \text{ W}}{2.45 \times 10^7 \text{ W}} = 0.82$$

For a plant with multiple units you can compute the overall efficiency by multiplying together the efficiencies of the individual components. As an example, assume that the conversion of fuel in a power plant yields 88 kJ in the steam product per 100 kJ of available energy from the coal being burned. Also assume that the conversion of the energy in the steam to mechanical energy is 43% efficient, and the conversion of the mechanical to electrical energy is 97% efficient. The overall efficiency is $(0.88)(0.43)(0.97) = 0.37$, meaning that two-thirds of the initial energy is dissipated as heat to the environment. These definitions provide a good way to compare process performance for energy conservation (but not the only way).

EXAMPLE 27.4 Calculation of Plant Efficiency

An analysis of energy usage takes place in all plants. This example uses data from M. Fehr, "An Auditor's View of Furnace Efficiency," in *Hydrocarbon Processing*, November, 1988, p. 93. Further details about the process equipment and energy auditing can be found in the article.

Figure E27.4 illustrates a gas-fired boiler. The data calculated from measurements on the heater were (all in kJ per m³ at SC of fuel gas):

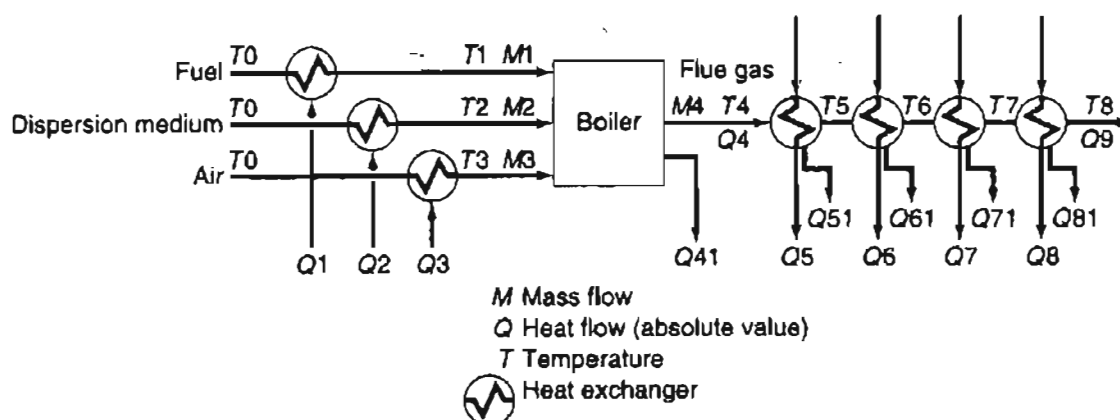


Figure E27.4

LHV of fuel:	36,654	Q_4 :	32,114
Q_1 :	16	Q_{41} :	6,988
Q_2 :	0	Q_8 :	1,948
Q_3 :	2,432	Q_9 :	2,643

Calculations from measurements gave values for sums of the other Q 's of

$$Q_5 + Q_6 + Q_7 = 9,092$$

$$Q_5 + Q_6 + Q_7 + Q_{51} + Q_{61} + Q_{71} = 27,119$$

$$Q_8 + Q_{81} = 2,352$$

From these heat transfer values, several efficiencies could be determined to evaluate plant performance:

(a) Gross efficiency

$$\frac{\text{LHV} + Q_1 + Q_2 + Q_3 - Q_9}{\text{LHV}} = \frac{36,654 + 16 + 0 + 2,432 - 2,643}{36,654} = 0.995$$

(b) Thermal efficiency

$$\frac{Q_5 + Q_6 + Q_7 + Q_8}{\text{LHV} + Q_1 + Q_2 + Q_3} = \frac{9,092 + 1,948}{36,654 + 16 + 0 + 2,432} = 0.282$$

(c) Combustion efficiency

$$\frac{Q_4}{Q_4 + Q_{41}} = \frac{32,114}{32,114 + 6,988} = 0.821$$

SELF-ASSESSMENT TEST

Questions

1. Together with the White House, a number of automobile company executives announced a program aimed at developing a new generation of automobiles with three times the fuel efficiency of existing cars. They said they were seeking "nothing less than a major, even radical breakthrough in automotive technology that can dramatically increase fuel efficiency, improve safety, and reduce emissions—while maintaining the affordability, performance, and utility of current comparable vehicles."

Is such a program possible?

2. Which is more efficient in heating water (a) an electric coffeepot, (b) a microwave oven, or (c) a pot on an electric stove?

Problems

1. A standard heating system in a standard house has the following characteristics: A gas furnace delivers energy to the living space at an average rate of 5.8 kW on a typical winter day. One-fourth of the energy that comes from the fuel input to the furnace is lost through incomplete combustion and the escape of heat to the outdoors via the flue. Of the remaining energy, 12% escapes through duct walls and doesn't reach the living space. Calculate the efficiency of the use of the gaseous fuel.
2. Cogeneration plants produce both electricity and steam. Figure SAT27.2P2 shows such a plant. What will be the percent fuel savings to get the electricity and steam from using the cogeneration plant in contrast to using two separate plants, one to produce 0.25 MJ of electric energy and one to produce 0.45 MJ of thermal energy in the steam?

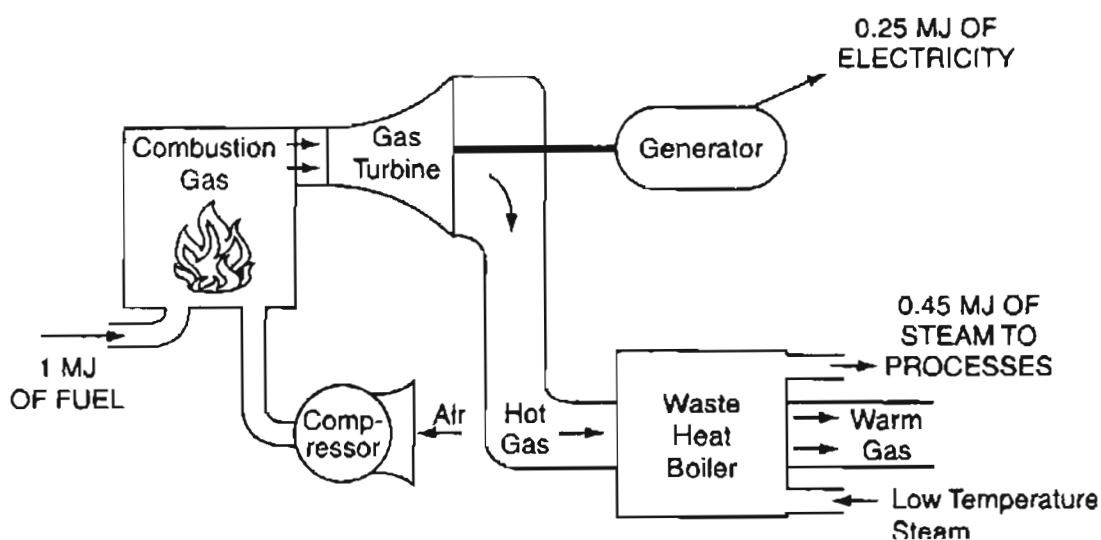


Figure SAT27.2P2

3. Calculate the reversible work required to compress 5 ft³ of an ideal gas initially at 100°F from 1 to 10 atm in an adiabatic cylinder. Such a gas has an equation of state $pV^{1.40} = \text{constant}$. Then calculate the actual work required if the efficiency of the process is 80%.

Thought Problems

1. A news announcement in a professional journal described a 20-hp Stirling engine that was going to be connected to and drive a 68-kW generator. Would you buy one of these at \$4500?
2. An author compared the effectiveness of gasoline-powered automobiles with electric-powered automobiles in terms of bbl of oil, as in the following table, and concluded that electric-powered vehicles overall were more efficient. Is the comparison valid?

Efficiencies	Gasoline (bbl of oil)	Electric (bbl of oil)
KWh equivalent	1700	1700
Refinery efficiency	74% to gasoline	89% to heavy oil
Distribution efficiency	95%	
Power generation efficiency		40%
Power distribution efficiency		91%
Battery efficiency		70%
Motor, drive train efficiency	14.7%	80%
KWh available	175.7	308.8
Vehicle weight	2400 lb	2800 lb
Road load: 50 mph, level	8.4 kW	10 kW
Distance traveled	1045 miles	1545 miles

3. A clipping from the *Wall Street Journal* reads:

Technical Disputes

Furnace efficiency is a comparison of the energy that goes into a furnace with the usable heat that comes out. Because oil furnaces use blowers to burn the fuel more efficiently and because oil produces less water vapor than gas, less heat is vented up the chimney, the Oil Jobbers Council says. The American Gas Association complains that such calculations ignore variations in oil quality that hurt efficiency. And it contends that oil furnaces are apt to "lose efficiency over time," while it says gas furnaces don't.

Which organization is correct, or is neither correct?

27.3 The Mechanical Energy Balance

You can never enter the same river twice.

Ancient Chinese proverb

Examine Figure 27.2. What size pump should be selected to remove biowaste from the collection tank? What pressure drop occurs between the collection tank drain and the pipeline to the treatment plant?

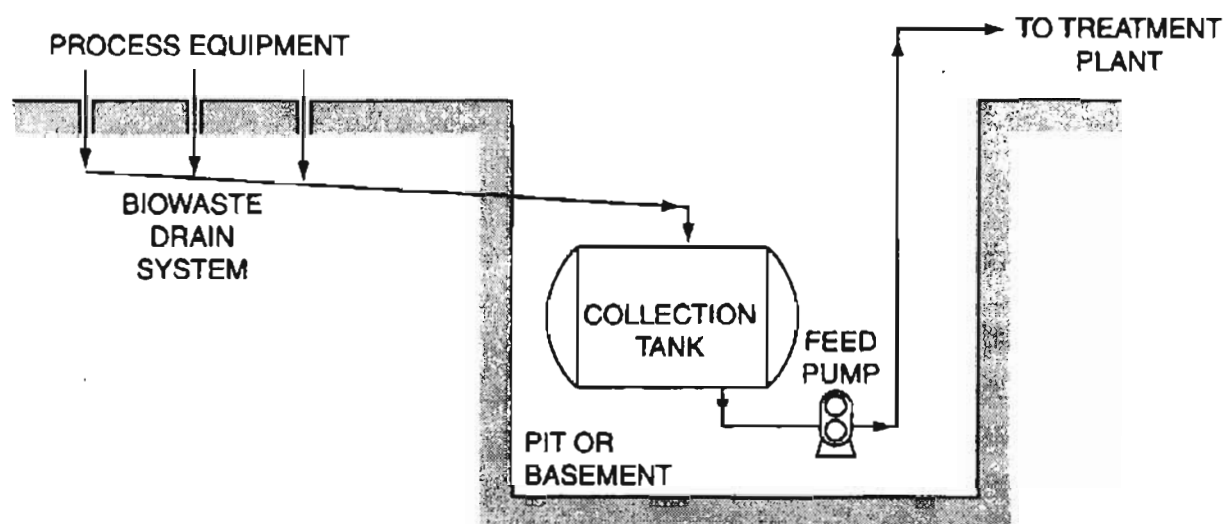


Figure 27.2 Biowaste collection system.

Such questions can be answered by using what is called the mechanical energy balance rather than the general energy balance.

In some processes, such as distillation columns or reactors, in which heat transfer and enthalpy changes are *the* important energy components in the energy balance, work, potential energy, and kinetic energy terms can be deemed to be zero or quite minor. However, in other processes, such as the compression of gases and pumping of liquids, work and the mechanical forms of energy are *the* important factors. For these processes, an energy balance, including solely the mechanical forms of energy, becomes a useful tool.

Two categories of energy of different “quality” can be distinguished:

- (a) the so-called *mechanical* forms of energy, such as kinetic energy, potential energy, and work, which are *completely* convertible by an *ideal* (reversible) engine from one form to another within the class.
- (b) other forms of energy, such as internal energy and heat, which are not so freely convertible.

Of course, as we explained in Section 27.1, in any real process with friction, viscous effects, mixing of components, and other dissipative phenomena taking place that prevent the complete conversion of one form of mechanical energy to another, allowances will have to be made in making a balance on mechanical energy for these “losses” in quality.

A balance on mechanical energy can be written on a microscopic basis for an elemental volume by taking the scalar product of the local velocity and the equation of motion.* After integration over the entire volume of the system, the *steady-state*

*Slattery, J. C. *Momentum, Energy, and Mass Transfer*, 2nd ed., Krieger, New York (1981).

mechanical energy balance for a system with mass interchange with the surroundings becomes, on a per unit mass basis

$$\Delta(\widehat{KE} + \widehat{PE}) + \int_{p_1}^{p_2} \hat{V} dp - \hat{W} + \hat{E}_v = 0 \quad (27.1)$$

where \widehat{KE} and \widehat{PE} are associated with the mass flow in and out of the system, and E_v represents the loss of mechanical energy, that is, the irreversible conversion by the *flowing fluid* of mechanical energy into nonmechanical forms of energy, a term that must in each individual process be evaluated by experiment (or, as occurs in practice, by use of already existing experimental results for a similar process). To integrate $\hat{V} dp$ you must know the relation between p and \hat{V} . A constant \hat{V} is the easiest case to integrate. Equation (27.1) is called the **Bernoulli equation** for a reversible process in which $\hat{E}_v = 0$. If the fluid is incompressible, and $W = 0$

$$\frac{\Delta p}{\rho} + \frac{\Delta v^2}{2} + g\Delta h = 0 \quad (27.2)$$

In Equation (27.2), if each term is divided by g , the units of the equation are those of Δh , and are known as “heads” of fluid. Thus, the 10 ft of water in Example 27.6 would be called a head of 10 feet of water.

A head of water is not a head full of water.

Anonymous

The mechanical energy balance is best applied in fluid-flow calculations when the kinetic and potential energy terms and the work are of importance, and the friction losses can be evaluated from handbooks with the aid of *friction factors* or *orifice coefficients*.

Let us now look at two typical applications of the steady-state mechanical energy balance.

EXAMPLE 27.5 . Comparison of the Reversible Work for a Batch Process with That of a Flow Process Operating Under the Same Conditions

Five cubic feet of an ideal gas at 100°F are to be compressed adiabatically from 1 atm to 10 atm. The equation of state to use for the gas is $pV^{1.40} = \text{constant}$. Two options exist for the compression.

- a. Compression in a horizontal cylinder with a piston, and
- b. Compression in a rotary compressor.

Calculate the reversible work required for the two alternate processes.

Solution**Process (a)**

You can represent this process as a closed system similar to Figure 27.1, but with the cylinder horizontal. The general energy balance reduces to

$$\Delta E = \Delta U = W$$

If you had a value for C_v you could integrate $C_v dT$ and get W , but no value is given for C_v (or C_p). However, you can calculate W by integrating $p dV$ for the reversible work, as shown in Examples 27.1 and 27.2.

Steps 1, 2, 3, and 4

You know the value of V_1 and have to calculate the value of V_2 . The system is the gas.

$$V_2 = V_1 \left(\frac{p_1}{p_2} \right)^{1/1.40} = 5 \left(\frac{1}{10} \right)^{1/1.40} = 0.965 \text{ ft}^3$$

Step 5

Basis: 5 ft³ of gas at 100°F and 1 atm

Steps 6–9

$$\begin{aligned} W_{\text{rev}} &= - \int_{V_1=5}^{V_2=0.965} p dV = - \int_{V_1}^{V_2} p_1 \left(\frac{V_1}{V} \right)^{1.40} dV = -p_1 V_1^{1.4} \int_{V_1}^{V_2} V^{-1.40} dV \\ &= - \frac{p_1 V_1^{1.40}}{1 - 1.40} (V_2^{-0.40} - V_1^{-0.40}) = - \frac{P_2 V_2 - p_1 V_1}{1 - 1.40} \\ &= - \frac{[(10)(0.965) - (1)(5)](\text{ft}^3)(\text{atm})}{-0.40} \left| \frac{1.987 \text{ Btu}}{0.7302(\text{ft}^3)(\text{atm})} \right. \\ &= 31.6 \text{ Btu (the positive sign indicates work done on the system.)} \end{aligned}$$

Process (b)

You can represent this process as an open, steady-state system, and apply the mechanical energy balance to solve for the reversible work

$$\Delta(\widehat{KE} + \widehat{PE}) + \int_{p_1}^{p_2} \hat{V} dp - \hat{W} + \hat{E}_v = 0$$

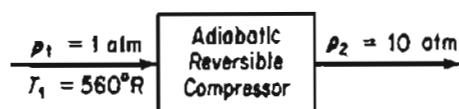


Figure E27.5

Figure E27.5 represents the process. The \widehat{KE} and \widehat{PE} terms are assumed to be zero, and $\hat{E}_v = 0$ because of the assumption of reversibility. Thus

$$\hat{W} = \int_{p_1}^{p_2} \hat{V} dp$$

Step 1, 2, 3, and 4

Figure E27.5 designates the system and data. The moles of gas are

$$n_1 = \frac{p_1 V_1}{RT_1} = \frac{1 \text{ atm} \left| \frac{5 \text{ ft}^3}{560^\circ\text{R}} \right| \frac{1 (\text{lb mol})(^\circ\text{R})}{0.7302 (\text{ft}^3)(\text{atm})}}{0.7302 (\text{ft}^3)(\text{atm})} = 0.0122 \text{ lb mol}$$

Step 5

$$\text{Basis} = 0.0122 \text{ lb mol}$$

Steps 3, 6, 7, 8, and 9

$$\begin{aligned} \hat{W}_{rev} &= \int_{p_1}^{p_2} \hat{V} dp = \int_{p_1}^{p_2} \hat{V}_1 \left(\frac{p_1}{p} \right)^{1/1.4} dp \\ &= \hat{V}_1 p_1^{0.714} [3.50(p_2^{0.286} - p_1^{0.286})] \end{aligned}$$

$$\begin{aligned} \hat{W}_{rev} &= n_1 \hat{W}_{rev} = n_1 \left(\frac{V_1}{n_1} \right) p_1^{0.714} [3.50(p_2^{0.286} - p_1^{0.286})] \\ &= (5)(1)^{0.714} [(3.50)(10)^{0.286} - 1^{0.286}] (\text{ft}^3)(\text{atm}) \left(\frac{1.987 \text{ Btu}}{0.7302 (\text{ft}^3)(\text{atm})} \right) \\ &= 44.4 \text{ Btu} \end{aligned}$$

EXAMPLE 27.6 Application of the Mechanical Energy Balance to the Pumping of Water

Calculate the work per minute required to pump 1 lb of water per minute from 100 psia and 80°F to 1000 psia and 100°F. The exit stream is 10 ft above the entrance stream.

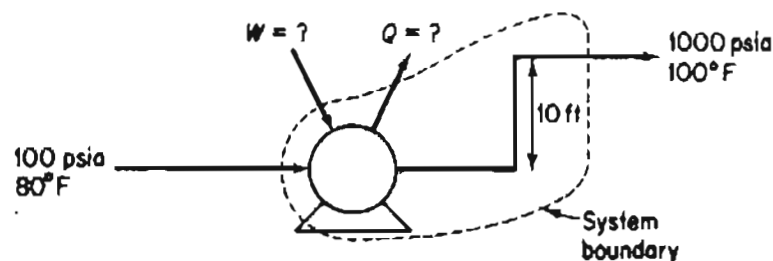


Figure E27.6

Solution

This problem is typical of many fluid flow problems.

Steps 1, 2, 3, and 4

The system shown in Figure E27.6 is a steady-state process and the data have been placed in the figure.

Steps 4, 6, and 7

The general mechanical energy balance is

$$\Delta(\widehat{KE} + \widehat{PE}) + \int_{p_1}^{p_2} \hat{V} dp - \hat{W} + \hat{E}_v = 0 \quad (a)$$

We assume that $\Delta\widehat{KE}$ is insignificant, that (preliminarily) the process is reversible so that $E_v = 0$, and that the pump is 100% efficient. (Subsequently, we will consider what to do if the process is not reversible.) Equation (a) reduces to

$$\hat{W} = \int_{p_1}^{p_2} \hat{V} dp + \Delta\widehat{PE} \quad (b)$$

Step 5

Basis: 1 min of operation = 1 lb H₂O

Steps 6 and 8

From the steam tables, the specific volume of liquid water is 0.01607 ft³/lb_m at 80°F and 0.01613 ft³/lb_m at 100°F. For all practical purposes the water is incompressible, and the specific volume can be taken to be 0.0161 ft³/lb_m. We have only one unknown in Equation (b): \hat{W} .

Step 9

$$\Delta\widehat{PE} = \frac{10 \text{ ft}}{\text{sec}^2} \left| \frac{32.2 \text{ ft}}{\text{sec}^2} \right| \frac{1 \text{ Btu}}{778(\text{ft})(\text{lb}_f)} = 0.0129 \text{ Btu/lb}_m$$

$$\int_{100}^{1000} 0.0161 dp = \frac{0.0161 \text{ ft}^3}{\text{lb}_m} \left| \frac{(1000 - 100)\text{lb}_f}{\text{in.}^2} \right| \left(\frac{12 \text{ in.}}{1 \text{ ft}} \right)^2 \frac{1 \text{ Btu}}{778(\text{ft})(\text{lb}_f)} = 2.68 \text{ Btu/lb}_m$$

$$\hat{W} = 2.68 + 0.0129 = 2.69 \frac{\text{Btu}}{\text{lb}_m}$$

About the same value can be calculated using the general energy balance (if $\hat{Q} = \widehat{KE} = 0$) and the steam tables, because the enthalpy change for a reversible

process for 1 lb of liquid water going from 100 psia and 100°F to 1000 psia is 2.70 Btu. Make the computation yourself. However, usually the enthalpy data for liquids other than water are missing, or not of sufficient accuracy to be valid, which forces you to turn to the mechanical energy balance.

You might now well inquire for the purpose of purchasing a pump-motor as to what the work would be for a real process instead of the fictitious reversible process assumed above. First, you would need to know the efficiency of the combined pump and motor so that the actual kW input from the surroundings (the electrical connection) to the system would be known. Second, the friction losses in the pipe, valves, and fittings must be estimated so that the term \hat{E}_v could be reintroduced into Equation (a). Suppose, for the purposes of illustration, that \hat{E}_v was estimated to be, from an appropriate handbook, 320 (ft)(lb_f)/lb_m and the pump-motor efficiency was 60% (based on 100% efficiency for a reversible pump-motor). Then,

$$\hat{E}_v = \frac{320(\text{ft})(\text{lb}_f)}{1 \text{ lb}_m} \left| \frac{1 \text{ Btu}}{778(\text{ft})(\text{lb}_f)} \right| = 0.41 \text{ Btu/lb}_m$$

$$\hat{W} = 2.68 + 0.013 + 0.41 = 3.10 \text{ Btu/lb}_m$$

Remember that the positive sign indicates that work is done on the system. The actual pump-motor must have the capacity.

$$\frac{3.10 \text{ Btu}}{\text{lb}} \left| \frac{1 \text{ lb}}{\text{min}} \right| \left| \frac{1}{0.60} \right| \left| \frac{1 \text{ min}}{60 \text{ sec}} \right| \left| \frac{1.415 \text{ hp}}{1 \text{ Btu/sec}} \right| = 0.122 \text{ hp}$$

SELF-ASSESSMENT TEST

Questions

1. What assumptions are built into Bernoulli's equation? Give two examples of a system where this equation would be useful.
2. Why can the terms in the Bernoulli equation be called heads?
3. Is the Bernoulli equation used more or less than the mechanical energy balance?
4. A textbook stated that "fluids can only flow from high pressure to low like electric charge can only flow from high potential to low." Is this true?
5. Explain why the flow out of a garden hose 10 m in length attached to the city water supply is more than the flow from a 100 m garden hose.

Problems

1. Water is pumped from a very large storage reservoir, as shown in the figure at the rate of 2000 gal/min. Determine the minimum power (i.e., that for a reversible process) required by the pump in horsepower.

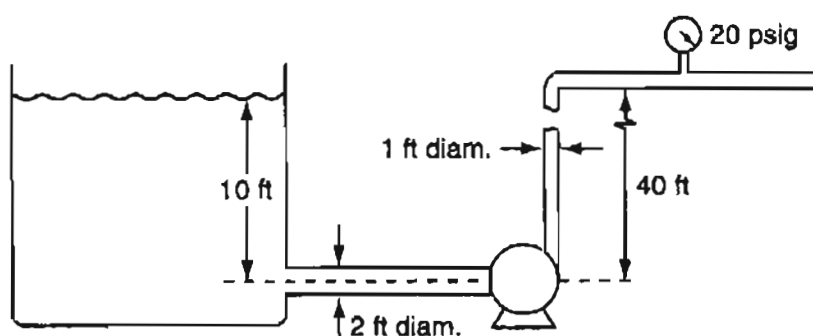


Figure P27.1SAT

2. Use the mechanical energy balance to explain why the flow of water down a vertical pipe that is full of water differs from the flow of water down a waterfall.
3. Fluid with a specific gravity of 1.15 drains from the bottom of a large open tank into a bucket through a 5 cm (inner diameter) pipe that terminates 4.5 m below the surface of the fluid in the tank. Calculate velocity of discharge of the fluid, ignoring frictional effects.

Thought Problems

1. Examine the Figure TP27.3P1. Is it possible by blowing in the stem of the funnel that the ping-pong ball will rise up toward the stem rather than fall down? Why?

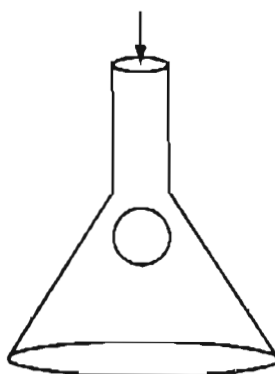


Figure TP27.3P1

2. Examine Figure TP27.3P2. List the figures that correctly represent the initial flow of water from the respective (full) columns.

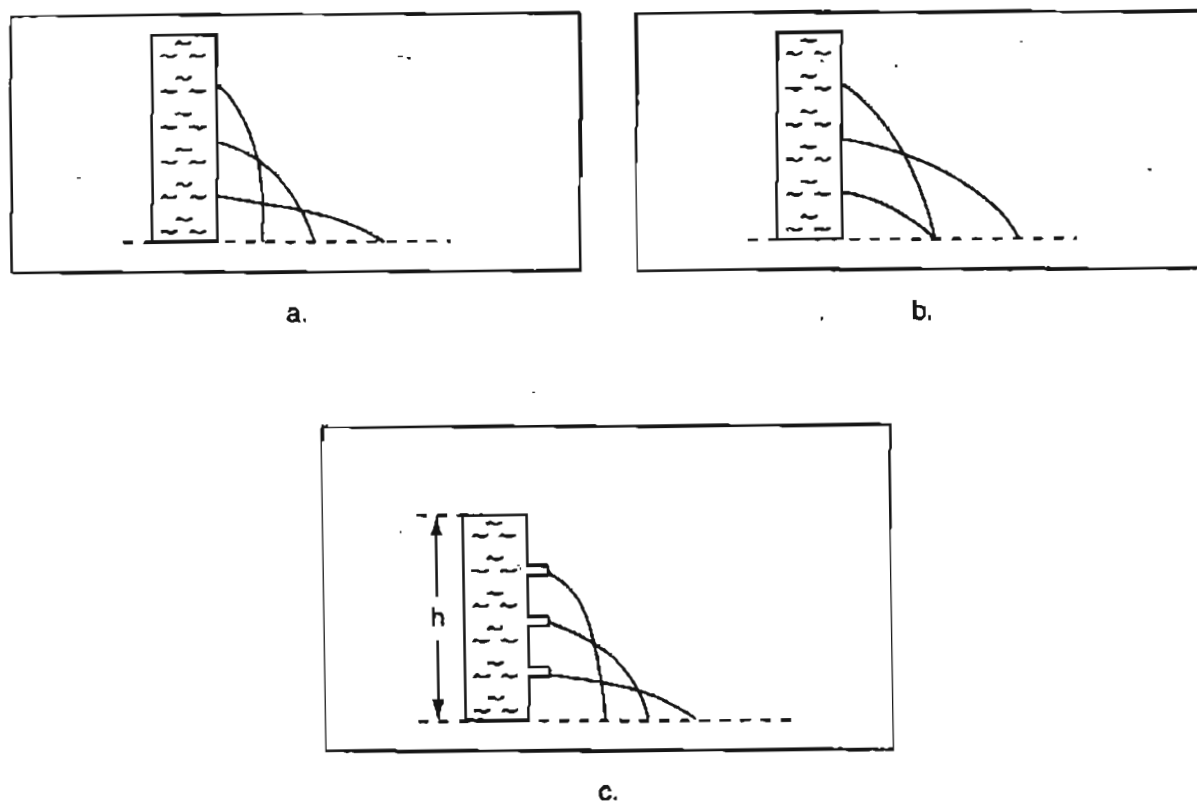


Figure TP27.3P2

Looking Back

In this chapter we explained the concepts of reversible (ideal) and irreversible processes. Process efficiency is a measure of how close to ideal a process is. We also added the mechanical energy balance to the list of tools you can use in analyzing processes, because it accounts for the conversions between mechanical forms of energy (KE , PE , W).

GLOSSARY OF NEW WORDS

Bernoulli equation The steady-state mechanical energy balance for a reversible process with no work.

Coefficient of performance (COP) The heat removed from a process divided by the work input to the process.

Efficiency The ratio of the work done by an organism or machine to the amount of food or fuel consumed and/or to the energy expended.

Efficiency, general The energy output divided by the energy input.

Heat engine efficiency The actual work output from a process divided by the heat input from a source.

Irreversible process A process that is not reversible.

Mechanical efficiency (a) The actual work output from a process divided by the work output if the process were reversible; or (b) the work input for a reversible process divided by the actual work input for the process.

Mechanical energy Type of energy that can be completely converted from one form to another.

Reversible process An idealized process in which changes occur under a differential imbalance in temperature, pressure, etc.

Universe The system plus its surroundings.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent. Also, most books on thermodynamics include one or more chapters on reversible processes.

Cengel, Y. A., and M. A. Boles. *Thermodynamics*, 4th ed. McGraw-Hill, New York (2002).

Fay, J. A., and D. Golomb. *Energy and the Environment*, Oxford University Press, Oxford (2002).

Glasstone, S. *Energy Deskbook*, Van Nostrand Reinhold, NY (1997).

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Moran, M. J. *Fundamentals of Engineering Thermodynamics*, 4th ed. John Wiley, New York (2000).

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<http://jchemed.chem.wisc.edu/Journals/issues/2002/Feb/abs193.html>

<http://www.mae.engr.ucf.edu/~aim/egn3343/Ch05/tsld009.htm>

<http://www.ccr.buffalo.edu/etomica/modules/pistoncylinder/Background1.html>

<http://scholar.chem.nyu.edu/0651/notes/pchem/node11.html>

<http://lorien.nci.ac.uk/ming/Webnotes/Main/CPE113.htm>

PROBLEMS

- *27.1** A phase change (condensation, melting, etc.) of a pure component is an example of a reversible process because the temperature and pressure remain constant during the

change. Calculate the work done in a batch process by butane when 1 kg of saturated liquid butane at 70 kPa vaporizes completely. Can you calculate the work done by the butane from the energy balance alone?

- *27.2** Calculate the work done when 1 lb mol of water in an open vessel evaporates completely at 212°F. Express your result in Btu.
- **27.3** One kilogram of steam goes through the following reversible process. In its initial state (state 1) it is at 2700 kPa and 540°C. It is then expanded isothermally to state 2, which is at 700 kPa. Then it is cooled at constant volume to 400 kPa (state 3). Next it is cooled at constant pressure to a volume of 0.4625 m³/kg (state 4). Then it is compressed adiabatically to 2700 kPa and 425°C (state 5), and finally it is heated at constant pressure back to the original state.
- Sketch the path of each step in a p - V diagram.
 - Compute ΔU and ΔH for each step and for the entire process.
 - Compute Q and W whenever possible for each step of the process.
- *27.4** Calculate the work done when 1 lb mol of water evaporates completely at 212°F in the following cases. Express your results in Btu/lb mol.
- A steady-state flow process: water flowing in a pipeline at 1 lb mol/min neglecting the potential and kinetic energy changes.
 - A nonflow process: water contained in a constant-pressure, variable-volume tank.
- **27.5** A question arose among a group of students concerning a gas expanding by an adiabatic process and at the same time doing no work. One part of the group thinks the process must be isothermal, while the other part insists it cannot be isothermal. They ask you to straighten this matter out.
- Explain under what circumstances the process will be isothermal.
 - Explain under what circumstances it will not be isothermal.
- **27.6** Nitrogen is being compressed by a piston as shown in Figure P27.6.

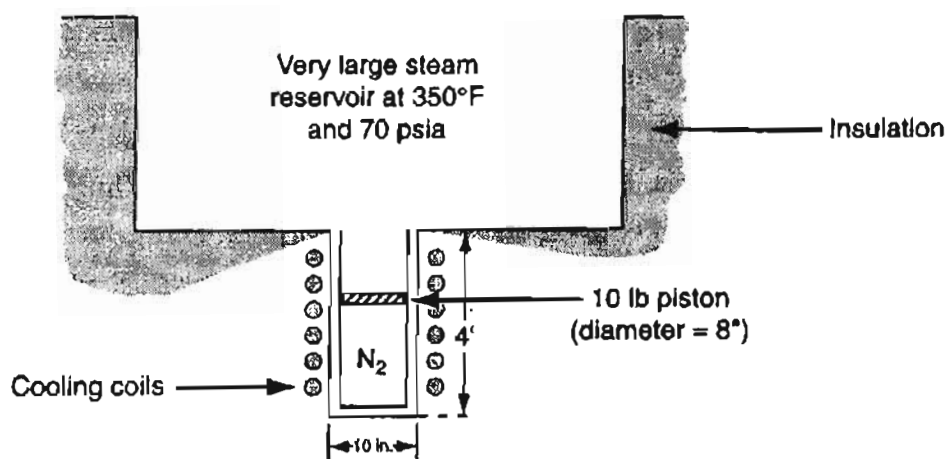


Figure P27.6

One lb mol of nitrogen is initially at 300°F and 14.7 psia in the cylinder. The piston is released and the N₂ compressed by the steam until the final volume of the

N_2 is $1/2$ the initial volume at which time the piston is caught and held in place. The barometric pressure is 740 mm. Calculate:

- (a) The work done by the steam
- (b) The work done on the N_2
- (c) The change in internal energy of the N_2 .

Assume throughout the problem that there is no heat transfer between the piston, cylinder, the steam, and the surroundings.

- *27.7 A motor is rated as 30 horsepower (hp). However, the output horsepower of the motor is only 24.6 hp. What is the efficiency of the motor?
- *27.8 Estimate the annual fuel cost for a 300-MW coal-fired power plant if the overall efficiency is 40% and the fuel cost is \$1.10/10⁶ Btu.
The plant operates for 6000 hr/year.
- *27.9 The following measurements have been made on a direct-fired heater using natural gas of the following composition

CH_4	96.4%
C_2H_6	2.01
C_3H_8	0.6
N_2	0.99

and 10.0% excess air.

Data: Flue gas temperature 450°C

Thermal heat loss 2% of LHV

Calculate the "efficiency" of the heater in percent

$$\text{efficiency} = 100 - \left(\frac{\text{thermal heat loss}}{\text{LHV}} - \frac{\text{enthalpy of flue gas relative to SC}}{\text{LHV}} \right) 100$$

- *27.10 Three efficiencies are commonly defined for a power plant such as shown in Figure P27.10:

$$\text{Boiler efficiency} = \frac{\text{Heat added to the steam}}{\text{Energy input from the fuel}}$$

$$\text{Gross plant efficiency} = \frac{\text{Gross electric output}}{\text{Energy input from the fuel}}$$

$$\text{Steam cycle efficiency} = \frac{\text{Gross electric output}}{\text{Heat added to the steam}}$$

Calculate these efficiencies based on the following data collected for one hour of operation of the plant in Figure P27.10:

Gas turbine is 500 MW

Steam flow rate was 640 kg/s

Water entered the boiler as saturated liquid at 150 kPa

Steam left the boiler superheated at 150 kPa and 530°C

The fuel (coal with an LHV of 28,400 kJ/kg) was burned at the rate of 64.6 kg/s

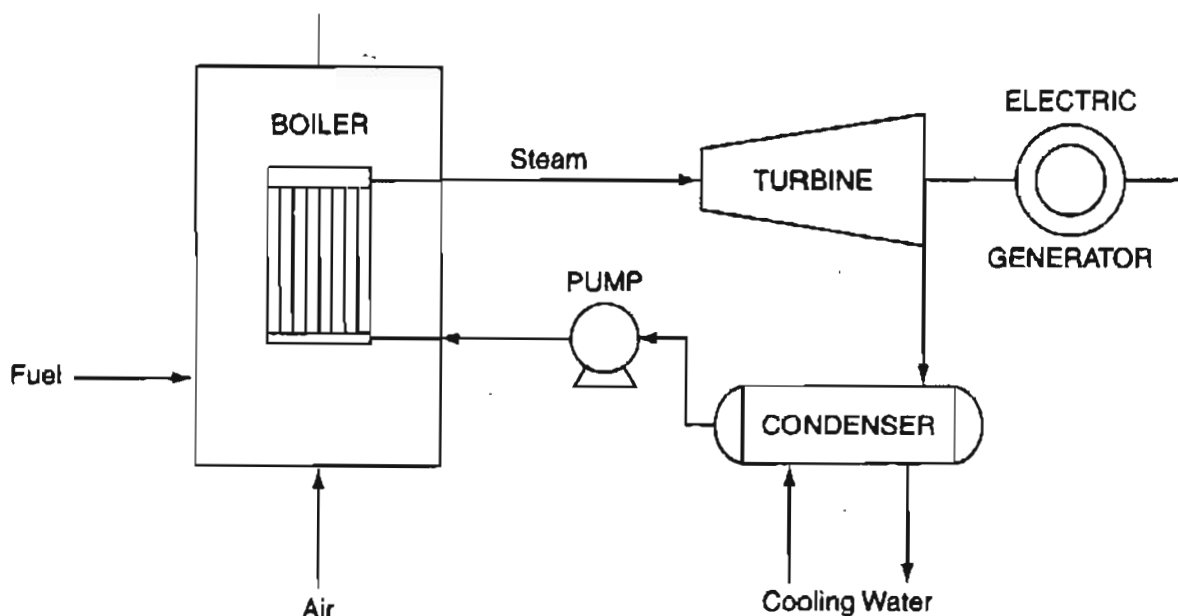


Figure P27.10

- *27.11 A system consists of 5 kg of water vapor at the dew point. The system is compressed isothermally at 400 K, and 400 kJ of work are done on the system by the surroundings. What volume of liquid was present in the system before and after compression?
- *27.12 In a processing plant, milk flows from a storage tank maintained at 5°C through a valve to a pasteurizer via an insulated 10-cm-diameter pipe at the rate of 1000 L/min. The upstream pressure is 290 kPa and downstream pressure is 140 kPa. Determine the lost work (E_v) in J/min and the temperature change which occurs in the milk as a result of this throttling process. (Milk and water are sufficiently equivalent in properties for you to use those of water.)
- *27.13 A power plant is as shown in Figure P27.13. If the pump moves 100 gal/min into the boiler with an overall efficiency of 40%, find the horsepower required for the pump. List all additional assumptions required.

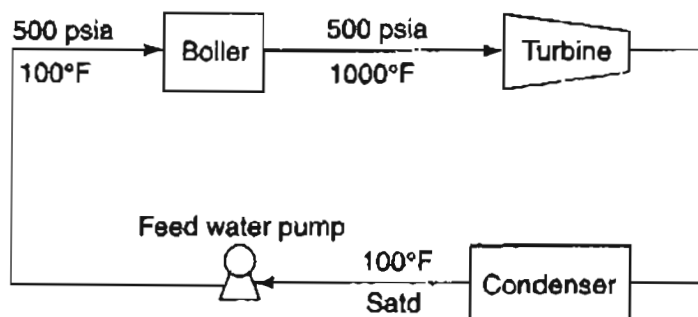


Figure P27.13

- *27.14 An office building requires water at two different floors. A large pipe brings the city water supply into the building in the basement level, where a booster pump is located. The water leaving the pump is transported by smaller insulated pipes to the

second and fourth floors, where the water is needed. Calculate the *minimum* amount of work per unit time (in horsepower) that the pump must do in order to deliver the necessary water, as indicated in Figure P27.14. (*Minimum* refers to the fact that you should neglect the friction and pump energy losses in your calculations.) The water does not change temperature.

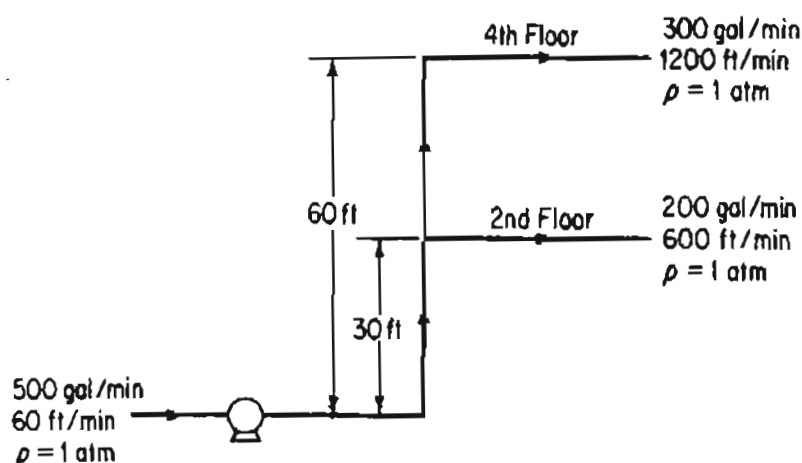


Figure P27.14

- *27.15 Water at 20°C is being pumped from a constant-head tank open to the atmosphere to an elevated tank kept at a constant pressure of 1150 kPa in an experiment as shown in Figure P27.15. If water is flowing in the 5.0-cm line at a rate of 0.40 m³/min, find

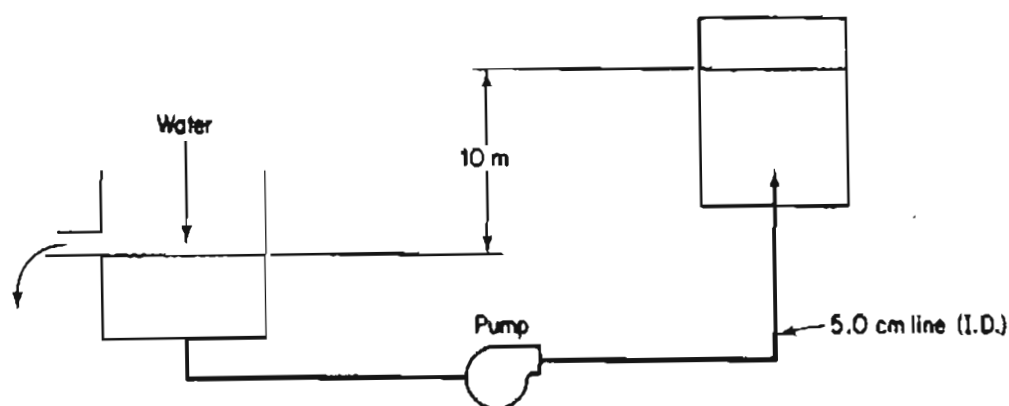


Figure P27.15

- The rating of the pump in joules per kilogram being pumped
- The rating of the pump in joules per minute

The pump and motor have an overall efficiency of 70% and the energy loss in the line can be determined to be 60.0 J/kg flowing.

- **27.16 An example in a book states that a pump is pumping finish water to a storage tank at 120 ft elevation difference. The pressure gauge reading at the discharge line of the pump is 87.6 psi. The problem was to determine the head loss due to friction.

The solution was:

$$\text{Gauge reading} = \text{elevation pressure} + \text{friction loss}$$

$$\begin{aligned}\text{Friction head loss} &= 87.6 \text{ psi} - 0.433 \text{ psi/ft} \times 120 \text{ ft} \\ &= 87.6 \text{ psi} - 53.0 \text{ psi} \\ &= 34.6 \text{ psi}\end{aligned}$$

Can the answer be correct for the E_v term in Equation (27.1)?

- *27.17** A boiler feedwater pump takes suction from a deareator that operates at 15 psig. To satisfy pump design requirements, the pressure at the suction of the pump must be 24 psig. It is known that \hat{E}_v , the irreversible energy loss due to pipe friction, is 4 (ft)(lb_f)/lb_m. The water velocity is 8 ft/s. What is the required height of the saturated water surface above the pump suction, in order to satisfy the 24 psig suction requirement?

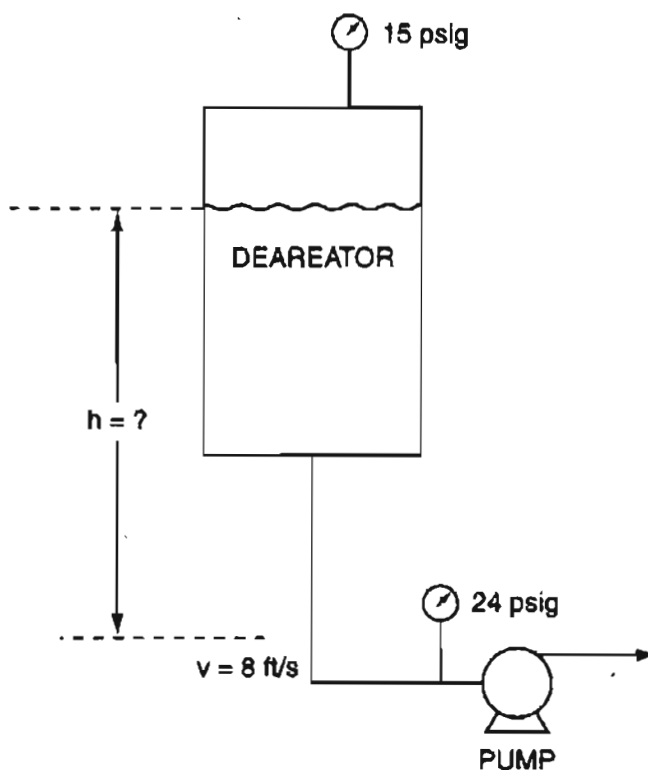


Figure P27.17

- *27.18** Solid carbon dioxide (dry ice) has innumerable uses in industry and in research. Because it is easy to manufacture, the competition is severe, and it is necessary to make dry ice very cheaply to be successful in selling it. In a proposed plant to make dry ice, the gaseous CO_2 is compressed isothermally and essentially reversibly from 6 psia and 40°F to a specific volume of 0.05 ft³/lb_m.
- What is the final state of the compressed CO_2 per lb?
 - Compute the work of compression.

- (c) What is the heat removed per lb CO₂?
- (d) If the actual efficiency of the compressor (relative to a reversible compressor) is 85 percent and the electricity to run the compressor motor costs \$0.08/kWh, what is the cost of compression of the solid CO₂ in dollars per pound of dry ice?
- *27.19** If a turbine, driven by water flowing from a reservoir 80 m higher than the turbine delivers 200 kW, what is the flow rate of the water in kg/s? Assume that the friction losses in the system yield an overall efficiency (actual work/ideal reversible work) of 75%. The reservoir is open to the atmosphere, and the exit velocity of the water is 5 m/s at a pressure of 150 kPa from the turbine.
- **27.20** A Venturi meter (refer to Figure 5.10) is a machine-cased section of pipe with a narrow throat. The device, in a short cylindrical section, consists of an entrance cone and a diffuser cone which expands to the full pipe diameter. Two openings are installed at the entrance (section 1) and at the throat (section 2). When the water passes through the throat, the velocity increases and the pressure decreases. The decrease of pressure is directly related to the flow. Use the Bernoulli equation and, neglecting friction loss, show that that the volumetric flow rate from the meter is

$$\dot{q} = C_d A_1 \sqrt{2[(\Delta p/\rho) + gZ]}$$

where \dot{q} = flow rate, m³/s

A_1 = cross-sectional areas at pipe exit, m²

g = gravity acceleration, 9.81 m/s²

$\Delta p = p_1 - p_2$ = pressure drop in Venturi tube, m

$Z = z_1 - z_2$ = difference of elevation head, m

C_d = coefficient of discharge (relation among the areas at throat and exit)

- *27.21** Leaks from process piping and oil or gas transmission lines can not only cause pollution, but can be extremely dangerous for combustible products if a source of ignition occurs. Based on the equation for the volumetric flow rate given in Problem 27.20, show that the mass flow rate of a fluid flowing in a pipe line can be measured by the meter using the equation

$$\dot{m} = C_d A \sqrt{2\rho \Delta p}$$

where Δp is in Pa

ρ is in kg/m³

C_d is the orifice coefficient (accounts for irreversibility)

\dot{m} is in kg/s

A = area of pipe, m²

Let $C_d = 0.65$, and calculate the mass flowrate of CH₄ at 30°C and 307 kPa from a leak with a diameter of 0.4 cm.

The pressure outside the pipe is 99 kPa.

CHAPTER 28

HEATS OF SOLUTION AND MIXING

28.1 Heats of Solution, Dissolution, and Mixing

865

28.2 Introducing the Effects of Mixing into the Energy Balance

872

Your objectives in studying this chapter are to be able to:

1. Distinguish between ideal solutions and real solutions.
2. Understand how energy changes occur on mixing.
3. Distinguish between integral heat of solution, differential heat of solution, heat of solution at infinite dilution, and heat of solution in the standard state.
4. Calculate the heat of mixing, or the heat of dissolution, at standard conditions given the moles of the materials forming the mixture and experimental data.
5. Calculate the standard integral heat of solution.
6. Apply an energy balance to problems in which the heat of mixing is significant.
7. Use an enthalpy-concentration chart in solving material and energy balances.

We have deferred consideration of the heat of solution/mixing until this chapter to avoid making the presentation of energy balances more complicated. But, in many processes, the energy involved when solution/mixing occurs is too large to be ignored. Recall from chemistry the warning “never add water to sulfuric acid, but slowly add the acid to water.”

Looking Ahead

In this chapter we explain how mixing and solution of one component in another to form a binary solution affect the energy balance. We focus only on binary mixtures here. You will learn several new terms and related calculations that affect the enthalpy terms in the general energy balance.

28.1 Heat of Solution, Dissolution, and Mixing

Up to this chapter we have assumed that when a stream consists of several components, the total properties of the stream are the appropriately weighted sum of the properties of the individual components. For such **ideal solutions**, we could write down for the heat capacity of an ideal mixture, for example

$$C_{p \text{ mixture}} = x_A C_{p_A} + x_B C_{p_B} + x_C C_{p_C} + \dots$$

or, for the enthalpy,

$$\Delta \hat{H}_{\text{mixture}} = x_A \Delta \hat{H}_A + x_B \Delta \hat{H}_B + x_C \Delta \hat{H}_C + \dots$$

In particular, mixtures of gases have been treated as ideal solutions.

However, you must take into consideration other types of mixtures. You can prepare various kinds of binary solutions or mixtures:

- a. gas – gas
- b. gas – liquid
- c. gas – solid
- d. liquid – liquid
- e. liquid – solid
- f. solid – solid

You can ignore the energy changes that occur on mixing for cases a, c, and f. They are negligible. The other mixtures comprise **real solutions**. When a gaseous or solid **solute** (the compound to be dissolved) is mixed with a liquid **solvent** (the compound in which the solute is dissolved), the energy effect that occurs is referred to as the **heat (really enthalpy) of solution**. When a liquid is mixed with a liquid, the energy effect is called the **heat (enthalpy) of mixing**. The negative of the heat of solution or mixing is the **heat (enthalpy) of dissolution**.

The heat of solution can be positive (endothermic) or negative (exothermic). Examine Figure 28.1, which shows the relative enthalpy values of a mixture of a fluorocarbon (C_6F_6) in benzene (C_6H_6).

You can treat heats of solution/mixing in the same way you treat chemical reactions. In the energy balance, you can (a) merge the heats of solution/mixing of the

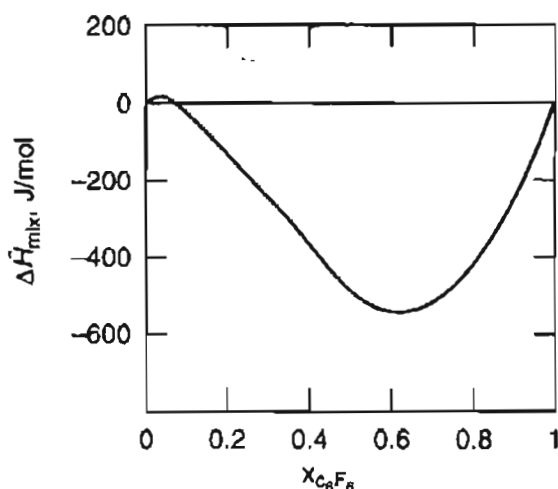
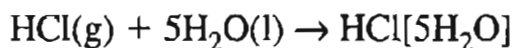


Figure 28.1 Relative enthalpy change on mixing C_6F_6 in C_6H_6 at 25°C .

compounds in the system with the heats of formation, or (b) consolidate the effects of the heats of solution/mixing in one lumped term analogous to a heat of reaction term. For example, let us represent the solution of 1 g mol $\text{HCl}(\text{g})$ into 5 g mol of $\text{H}_2\text{O}(\text{l})$ by the following chemical equation:



If you carry out experiments to measure the heat transfer from an apparatus at a constant 25°C and 1 atm by successively adding water to HCl , and arrange the experiments so that the energy balance reduces to $Q = \Delta H$, then the values of ΔH would be the tabulation in the third column of Table 28.1 below. (The values incorporate a slight adjustment in the measured values of Q at the vapor pressure of the solution to adjust them to 1 atm, the standard state.) If you cumulate each incremental change in ΔH , you would obtain the fourth column in Table 28.1. Appendix H and the CD that accompanies this book contain other tables listing the heats of solution for common compounds. Table 28.1 shows that there are actually two concepts that incorporate the name “heat of solution”: (a) The **incremental (differential) heat of solution**, column 3; and (b) the **integral heat of solution**, column 4—the heat of solution for the combination of 1 mole of $\text{HCl}(\text{g})$ with n moles of $\text{H}_2\text{O}(\text{l})$.

Usually “heat of solution” refers to concept b, and **the enthalpy change is stated per mole of solute**.

Figure 28.2 is a plot of the values listed in column 4 of Table 28.1. The asymptotic value of the heat of solution of HCl dissolved in an infinite amount of water is known as the **heat of solution at infinite dilution** ($-75,144 \text{ J/g mol HCl}$).

If you want to calculate the heat of formation of any of the solutions of $\text{HCl}(\text{g})$ in $\text{H}_2\text{O}(\text{l})$, all you have to do is add the heat of solution to the heat of formation of $\text{HCl}(\text{g})$, as shown in column 5 in Table 28.1

$$\Delta \hat{H}_{f,\text{solution}}^\circ = \Delta \hat{H}_{f,\text{solute}}^\circ + \Delta \hat{H}_{\text{solution}}^\circ \quad (28.1)$$

TABLE 28.1 Heat of Solution Data at 25°C and 1 atm

Composition	Total moles H ₂ O added to 1 mole HCl	$\Delta\hat{H}^\circ$ for each incremental step (J/g mol HCl)	Integral heat of solution (cumulative $\Delta\hat{H}^\circ$) (J/g mol HCl)	Heat of formation $\Delta\hat{H}_f^\circ$ (J/g mol HCl)
HCl(g)	0			-92,311
HCl[1H ₂ O(aq)]	1	-26,225	-26,225	-118,536
HCl[2H ₂ O(aq)]	2	-22,593	-48,818	-141,129
HCl[3H ₂ O(aq)]	3	-8,033	-56,851	-149,161
HCl[4H ₂ O(aq)]	4	-4,351	-61,202	-153,513
HCl[5H ₂ O(aq)]	5	-2,845	-64,047	-156,358
HCl[8H ₂ O(aq)]	8	-4,184	-68,231	-160,542
HCl[10H ₂ O(aq)]	10	-1,255	-69,486	-161,797
HCl[15H ₂ O(aq)]	15	-1,503	-70,989	-163,300
HCl[25H ₂ O(aq)]	25	-1,276	-72,265	-164,576
HCl[50H ₂ O(aq)]	50	-1,013	-73,278	-165,589
HCl[100H ₂ O(aq)]	100	-569	-73,847	-166,158
HCl[200H ₂ O(aq)]	200	-356	-74,203	-166,514
HCl[500H ₂ O(aq)]	500	-318	-74,521	-166,832
HCl[1000H ₂ O(aq)]	1,000	-163	-74,684	-166,995
HCl[50,000H ₂ O(aq)]	50,000	-146	-75,077	-167,388
HCl[∞H ₂ O]		-67	-75,144	-167,455

SOURCE: National Bureau of Standards Circular 500, U.S. Government Printing Office, Washington, D.C., 1952.

where $\Delta\hat{H}_{\text{solution}}^\circ$ is the integral heat of solution at standard conditions per mol of HCl, and $\Delta\hat{H}_{f,\text{solution}}^\circ$ is the heat of formation of the solution itself per mol of HCl. It is important to remember that **the heat of formation of the H₂O does not enter into the calculation** in Equation (28.1); it is defined as zero for the process of solution. Tables in reference books usually list data for the heats of formation of solutions in the standard state rather than the heats of solution themselves. In the processes and examples below, we assume that the systems are open, steady state,

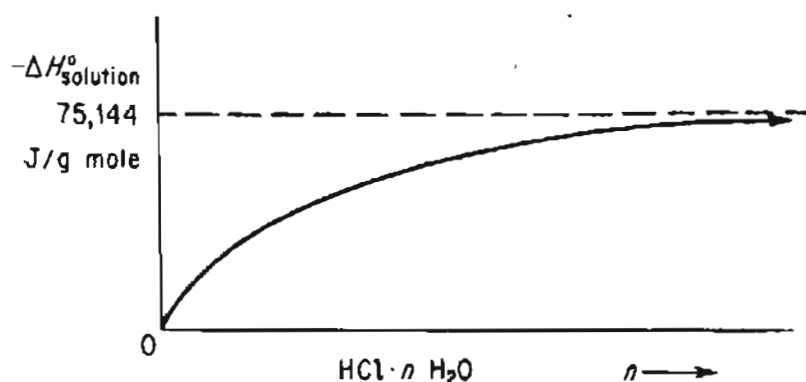


Figure 28.2 Integral heat of solution of HCl in water.

or, if closed, that the accumulation term in the energy balance is $\Delta U = \Delta H$ so that we discuss only enthalpies.

You can treat a solution as a single compound in making calculations in an energy balance by using the property that enthalpies of solutions are state variables. One convenient procedure is to merge the heats of solution of a compound with the heats of formation, as indicated in column 5 of Table 28.1 and by Equation (28.1). Then the specific enthalpy of a solution relative to SC would be

$$\hat{H}_{\text{solution}}(T) = \Delta \hat{H}_{f,\text{solution}}^{\circ} + [\hat{H}(T) - \hat{H}(\text{SC})]_{\text{solution}} \quad (28.2)$$

where the term in the brackets represents the sensible heat of the solution itself (any phase change is unlikely).

For example, suppose you want to find the $\Delta \hat{H}_{\text{solution}}^{\circ}$ that occurs at SC when a solution of 1 g mol of HCl dissolved in 1 g mol of H_2O is placed in an infinite amount of water. Use the data listed in column 5 of Table 28.1, and subtract the enthalpy of the initial state from the enthalpy of the final state as follows:

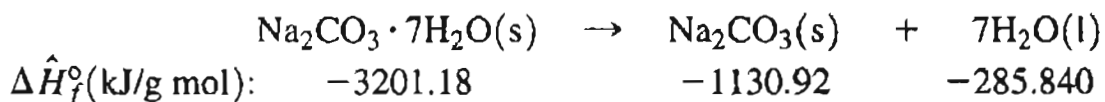
$$(-167,455) - (-118,536) = -48,911 \text{ J/g mol HCl}$$

As another example, consider a process in which a dilute solution of HCl is to be concentrated. Because enthalpy changes for heats of solution are state variables, you can easily use the integral heats of solution of HCl solutions at their respective concentrations. Then you can calculate the enthalpy change between the final and initial states for a closed process, or the enthalpy change between the output and the input for a flow process. Thus, if you mix 1 mole of HCl[15 H_2O] and 1 mole of HCl[5 H_2O], you obtain 2 moles of HCl[10 H_2O], and the total enthalpy change at 25°C and 1 atm is (using column 4 of Table 28.1 as an alternate to column 5)

$$\begin{aligned} \Delta H^{\circ} &= [2(-69,486)] - [1(-70,989) + 1(-64,047)] \\ &= -3936 \text{ J} \end{aligned}$$

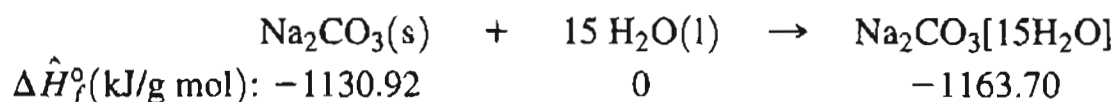
You would have to remove 3936 J to keep the temperature of the final mixture at 25°C . The same value for ΔH° would be obtained using the data in column 5.

We should mention that the solution of a hydrated salt such as $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ requires a little care in the calculations. If you mix the hydrated salt with water or a CaCl_2 solution, the procedure to calculate the enthalpy change is as follows. You first have to decompose (melt) the hydrated salt into a solid and water. Then you dissolve the total salt available into the total water available after the melting and solution. For example, from the data in Problem 28.3, if 1 g mol of $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ is dissolved in 8 g mol of $\text{H}_2\text{O}(l)$, the resulting solution contains 1 g mol of Na_2CO_3 and 15 g mol of H_2O . The melting step involves the following enthalpy change:



$$\Delta H^\circ = [7(-285.840) + 1(-1130.92)] - [1(-3201.18)] = +69.38 \text{ kJ}$$

The solution step is:



$$\Delta H^\circ = (-1163.70) - (-1130.92) = -32.78 \text{ kJ}$$

The overall enthalpy change is $69.38 - 32.78 = 36.60 \text{ kJ}$.

EXAMPLE 28.1 Application of Heat of Solution Data

You are asked to prepare an ammonium hydroxide solution at 77°F by dissolving gaseous NH_3 in water. Calculate

- The amount of cooling needed in Btu to prepare a 3.0% solution containing 1 lb mol of NH_3 .
- The amount of cooling needed in Btu to prepare 100 gal of a solution of 32.0% NH_3 .

Data: The following heat of solution data have been taken from NBS circular 500.

Composition	State	$-\Delta \hat{H}_f^\circ$ (Btu/lb mol)	$-\Delta \hat{H}_{\text{soln}}^\circ$ (Btu/lb mol)
	g	19,900	0
1 mol H_2O	aq	32,600	12,700
2 H_2O	aq	33,600	13,700
3 H_2O	aq	34,000	14,100
4 H_2O	aq	34,200	14,300
5 H_2O	aq	34,350	14,450
10 H_2O	aq	34,600	14,700
20 H_2O	aq	34,700	14,800
30 H_2O	aq	34,700	14,800
40 H_2O	aq	34,700	14,800
50 H_2O	aq	34,750	14,850
100 H_2O	aq	34,750	14,850
200 H_2O	aq	34,800	14,900
$\infty \text{ H}_2\text{O}$	aq	34,800	14,900

Solution

The solution will be presented in abbreviated form.

Reference temperature: 77°F

a. Basis: 1 lb mol $\text{NH}_3 \equiv 17 \text{ lb NH}_3$

$$\text{wt. \% NH}_3 = \frac{\text{lb NH}_3}{\text{lb H}_2\text{O} + \text{lb NH}_3} (100)$$

$$3 = \frac{17(100)}{17 + m_{\text{H}_2\text{O}}} \quad m_{\text{H}_2\text{O}} = 550 \text{ lb or about } 30 \text{ lb mol H}_2\text{O}$$

From the table above, the $\Delta \hat{H}_{\text{soln}}^\circ = -14,800 \text{ Btu/lb mol NH}_3$, which is equal to 14,800 Btu removed from the system.

b. Basis: 100 gal solution

From Lange's *Handbook of Chemistry*, a 32.0% solution of NH_3 has the following properties

	NH_3	H_2O
sp.gr.:	0.889	1.003

The density of the 32.0% solution in lb/100 gal is

$$\frac{(0.889)(62.4)(1.003)(100)}{7.48} = 744 \text{ lb/100 gal}$$

$$\frac{744(0.32)}{17} = 14.0 \text{ lb mol NH}_3/100 \text{ gal solution}$$

Basis: 1 lb mol NH_3

$$32.0 = \frac{1700}{17 + m_{\text{H}_2\text{O}}} \quad m_{\text{H}_2\text{O}} = 36 \text{ lb and } n_{\text{H}_2\text{O}} = 2 \text{ lb mol}$$

$$\left. \begin{array}{l} \text{Cooling req'd} \\ \text{Btu/100 gal} \end{array} \right\} = \left(\frac{\text{lb mol NH}_3}{100 \text{ gal}} \right) \left(-\Delta \hat{H}_{\text{soln}}^\circ \frac{\text{Btu}}{\text{lb mol NH}_3} \right)$$

$$\left. \begin{array}{l} \text{Cooling req'd} \\ \text{for 100 gal} \\ \text{32.0\% NH}_3 \text{ Soln} \end{array} \right\} = (14.0)(-13,700) = -192,000 \text{ Btu/100 gal soln (heat removed)}$$

SELF-ASSESSMENT TEST

Questions

- Define and show on a sketch the
 - integral heat of solution
 - differential heat of solution
- Answer the following questions true or false:
 - Heats of reaction and heats of solution represent the same physical phenomena.

- b. All mixtures have significant heats of solution.
 - c. The heat of mixing at infinite dilution involves an infinite amount of solvent.
 - d. Heats of solution can be positive and negative.
 - e. A gas mixture is usually an ideal solution.
3. a. What is the reference state for H_2O in the table for the heat of solution of HCl ?
b. What is the value of the enthalpy of the H_2O in the reference state?
4. Repeat Question #3 for HCl .

Problems

1. Calculate the heat of solution at standard conditions when 1 mol of a solution of 20 mole % HCl is mixed with 1 mol of a solution of 25 mole % HCl .
2. How much heat has to be added to a solution of 1 g mol of HCl in 10 g mol of H_2O to concentrate the solution to 1 g mol HCl in 4 g mol H_2O ?
3. The heat of formation of H_2SO_4 is $\sim 811.319 \text{ kJ/g mol H}_2\text{SO}_4$. What is the heat of formation per g mol of H_2SO_4 of a solution of 20% sulfuric acid? Use Appendix H.

Thought Problems

1. A tanker truck of hydrochloric acid was inadvertently unloaded into a large storage tank used for sulfuric acid. After about one-half of the 3000-gal load had been discharged, a violent explosion occurred, breaking the inlet and outlet lines and buckling the tank. What might be the cause of the explosion?
2. A concentrated solution (73%) of sodium hydroxide was stored in a vessel. Under normal operations, the solution was forced out by air pressure as needed. When application of air pressure did not work, apparently due to solidification of the caustic solution, water was poured through a manhole to dilute the caustic and free up the pressure line. An explosion took place and splashed caustic out of the manhole 15 ft into the air. What caused the incident?

Discussion Problem

1. A significant amount of energy is liberated when freshwater and saltwater are mixed. It has been calculated that the dilution of a cubic meter of freshwater per second in a large volume of sea water dissipates roughly 2.3 megawatts of power. If this energy could be put to use rather than heating the ocean, it is estimated that the potential of the flow of the Columbia River would yield 15,000 MW. The technology to collect such potential has been proposed, namely to use a selective membrane that lets certain molecules through but holds others back. Instead of separating water from saltwater by imposing an electric potential on the membrane as in desalinization, the idea is to reverse the process and mix freshwater with saltwater to generate an electric current. The membranes are arranged so that positive ions flow in one direction and negative ions in the other direction. What do you think of the proposal?

28.2 Introducing the Effects of Mixing into the Energy Balance

In Section 28.1 we restricted the discussion and examples to the standard state (25°C and 1 atm). In this section we proceed with what happens when the temperatures of the inlet and outlet streams differ from 25°C for a binary mixture in an open, steady-state process. (For a closed system the initial and final states of the internal energy would be involved rather than the stream flows.) You can treat problems involving the heat of solution/mixing in exactly the same way that you can treat problems involving reaction. The heat of solution/mixing is analogous to the heat of reaction in the energy balance. You can carry out the needed calculations by

- (a) associating heats of formation of the compounds and solutions with each of the respective compounds and solutions, or
- (b) computing the overall lumped heat of solution at the reference state,

and for either option calculating the sensible heats (and phase change effects) for the compounds and solutions from the reference state.

The next example shows the detailed procedure.

EXAMPLE 28.2 Application of Heat of Solution Data

Hydrochloric acid is an important industrial chemical. To make aqueous solutions of it in a commercial grade (known as *muratic acid*), purified $\text{HCl}(\text{g})$ is absorbed in water in a tantalum absorber in a steady-state continuous process. How much heat must be removed from the absorber by the cooling water per 100 kg of product if hot $\text{HCl}(\text{g})$ at 120°C is fed into water in the absorber as shown in Figure E28.2? The feed water can be assumed to be at 25°C , and the exit product $\text{HCl}(\text{aq})$

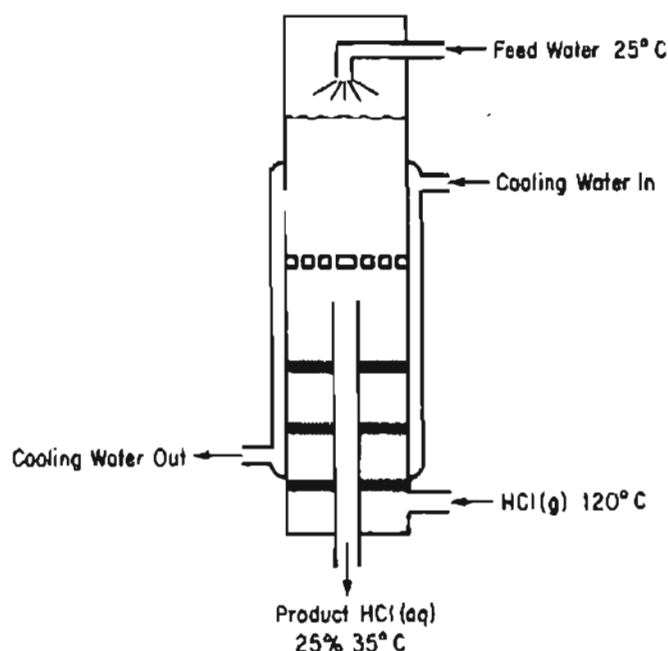


Figure E28.2

is 25% HCl (by weight) at 35°C. The cooling water does not mix with the HCl solution.

Solution

Steps 1, 2, 3, and 4

You need to convert the process data to moles of HCl to be able to use the data in Table 28.1. Consequently, we will first convert the product into moles of HCl and moles of H₂O.

TABLE E28.2a

Component	kg	Mol. wt.	kg mol	Mole fraction
HCl	25	36.37	0.685	0.141
H ₂ O	75	18.02	4.163	0.859
Total	100		4.848	1.000

The mole ratio of H₂O to HCl is $4.163/0.685 = 6.077$. The MW of the solution is 20.60.

Step 5

The system will be the HCl and water (not including the cooling water).

Basis: 100 kg of product

Ref. temperature: 25°C

Steps 6 and 7

The energy balance reduces to $Q = \Delta H$, and both the initial and final enthalpies of all of the streams are known or can be calculated directly, hence the problem has zero degrees of freedom. From simple material balances the kg and moles of HCl in and out and the water in and out are as listed in Table E28.2a above.

Step 3 (continued)

Next, you have to determine the enthalpy values for the streams. Data are: C_p for the HCl(g) is from Table E.1; C_p for the product is approximately 2.7 J/(g)(°C) equivalent to 55.6 J/(gmol) (°C); $\Delta \hat{H}_f^\circ$ for HCl · 6.077 H₂O = -157,753 J/g mol HCl. We will use $\Delta \hat{H}_f^\circ$ values for each stream in the calculation of ΔH .

Steps 8 and 9

TABLE E28.2b

Stream	g mol	T(°C)	\hat{H}_f° (J/g mol HCl)	$\Delta \hat{H}_{\text{sensible}}$ (J/g mol)
<i>OUT</i>				
HCl (aq)	4.848*	35	-157,753	$\int_{25^\circ\text{C}}^{35^\circ\text{C}} (55.6) dT = 27$
<i>IN</i>				
H ₂ O(l)	4.163	25	-	0
HCl(g)	0.685	120	-92,311	$\int_{25^\circ\text{C}}^{120^\circ\text{C}} (29.13 - 0.134 \times 10^{-2} T) dT = 2,758$

*HCl=0.685

$$Q = \Delta H_{\text{out}} - \Delta H_{\text{in}}$$

$$= [0.685(-157,753) + 4.848(55.6)(35 - 25)] - [0 + 0.685(-92,311) + 0.685(2758)]$$

$$= -42,370 \text{ J}$$

If you use heat of solution values, the calculation is (from Table 28.1 the heat of solution is -65,442 J/g mol HCl for the ratio of HCl/H₂O = 6.077)

$$Q = \Delta H_{\text{out, sensible}} - \Delta H_{\text{in, sensible}} + \Delta H_{\text{solution}}$$

$$= (4.848)(55.6)(35 - 25) - [0.685(2753) + 0] + (0.685)(-65,442)$$

$$= -42,370 \text{ J as expected}$$

In a process simulation code, table lookup or equations would be used to calculate the heats of formation at various temperatures (and pressures) other than 25°C (and 1 atm). The details would be buried in the computer code. You can better understand what the calculations for an energy balance involve if you use a graph—at the expense of some accuracy—versus using equations.

A convenient graphical way to represent enthalpy data for binary solutions is via an **enthalpy-concentration diagram**. Enthalpy-concentration diagrams (*H-x*) are plots of specific enthalpy versus concentration (usually mass or mole fraction) with temperature as a parameter. Figure 28.3 illustrates one such plot. If available,*

*For a literature survey as of 1957, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke. *Chem. Eng. Data Ser.*, 2, 32 (1957). Additional references: for CCl₄, see M. M. Krishniah et al. *J. Chem. Eng. Data*, 10, 117 (1965); for EtOH-EtAc, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke. *Br. Chem. Eng.*, 10, 703 (1965); for methanol-toluene, see C. A. Plank and D. E. Burke. *Hydrocarbon Process*, 45, 8, 167 (1966); for acetone-isopropanol, see S. N. Balasubramanian. *Br. Chem. Eng.*, 12, 1231 (1967); for acetonitrile-water-ethanol, see Reddy and Murti. *ibid.*, 13, 1443 (1968); for alcohol-aliphatics, see Reddy and Murti. *ibid.*, 16, 1036 (1971); and for H₂SO₄, see D. D. Huxtable and D. R. Poole. *Proc. Int. Solar Energy Soc.*, Winnipeg, August 15, 1976, 8, 178 (1977). For more recent sources search the Internet.

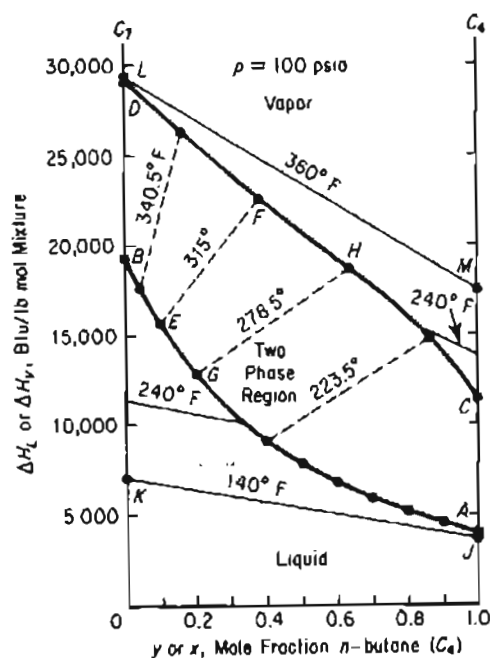


Figure 28.3 Enthalpy concentration of *n*-butane-*n*-heptane at 100 psia. Curve DFHC is the saturated vapor; curve BEGA is the saturated liquid. The dashed lines are equilibrium tie lines connecting y , the mole fraction of C_4 in the vapor, and x , the mole fraction of C_4 in the liquid, at the same temperature.

such charts are useful in making combined material and energy balance calculations in distillation, crystallization, and all sorts of mixing and separation problems. You will find a few examples of enthalpy-concentration charts in Appendix I.

As you might expect the preparation of an enthalpy concentration chart requires numerous calculations and valid enthalpy or heat capacity data for solutions of various concentrations. Refer to *Unit Operations of Chemical Engineering* (W. L. McCabe and J. C. Smith, 3rd ed., McGraw-Hill, New York [1976]) for instructions if you have to prepare such a chart. In the next example we show how to use an H - x chart.

EXAMPLE 28.3 Application of an Enthalpy-Concentration Chart

Six hundred pounds of 10% NaOH per hour at 200°F are added to 400 lb/hr of 50% NaOH at the boiling point in an insulated vessel. Calculate the following:

- The final temperature of the exit solution.
- The final concentration of the exit solution.
- The pounds of water evaporated per hour during the process.

Solution

You can use the steam tables and the NaOH- H_2O enthalpy-concentration chart in Appendix I as your sources of data. What are the reference conditions for the chart? The reference conditions for the latter chart are $\Delta \hat{H} = 0$ at 32°F for pure liquid water, an infinitely dilute solution of NaOH. Pure caustic has an enthalpy at 68°F of 455 Btu/lb above this datum. Treat the process as a flow process even if is not. The energy balance reduces to $\Delta H = 0$. Basis: 1000 lb of final solution = 1 hr

You can write the following material balances:

<u>Component</u>	<u>10% solution</u>	+	<u>50% solution</u>	=	<u>Final solution</u>	<u>wt%</u>
NaOH	60		200		260	26
H ₂ O	540		200		740	74
Total	600		400		1000	100

Enthalpy data from the H - x chart

	<u>10% solution</u>	<u>50% solution</u>
$\Delta \hat{H}$ (Btu/lb):	152	290

The energy balance is

<u>10% solution</u>		<u>50% solution</u>		<u>Final solution</u>
600(152)	+	400(290)	=	ΔH
91,200	+	116,000	=	207,200

Note that the enthalpy of the 50% solution at its boiling point is taken from the bubble point at $\omega_{\text{NaOH}} = 0.50$. The enthalpy per pound of the final solution is

$$\frac{207,200 \text{ Btu}}{1000 \text{ lb}} = 207 \text{ Btu/lb}$$

On the enthalpy-concentration chart for NaOH-H₂O, for a 26% NaOH solution with an enthalpy of 207 Btu/lb, you would find that only a two-phase mixture of (1) saturated H₂O vapor and (2) NaOH-H₂O solution at the boiling point would exist. To get the fraction H₂O vapor, you have to make an additional energy (enthalpy) balance. By interpolation, draw the tie line through the point $x = 0.26$, $H = 207$ (make it parallel to the 220° and 250°F tie lines). The final temperature of the tie line appears from Figure E28.3 to be 232°F; the enthalpy of the liquid at the bubble point at this temperature is about 175 Btu/lb. The enthalpy of the saturated water vapor (no NaOH is in the vapor phase) from the steam tables at 232°F is 1158 Btu/lb. Let x = lb of H₂O evaporated.

Basis: 1000 lb of final solution

$$x(1158) + (1000 - x) 175 = 1000 (207.2)$$

$$x = 32.8 \text{ of H}_2\text{O evaporated/hr}$$

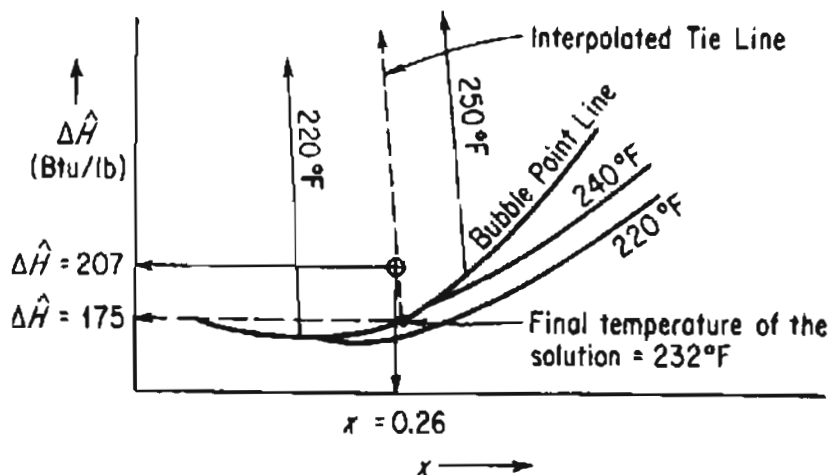


Figure E28.3

SELF-ASSESSMENT TEST

Questions

1. Is a gas mixture an ideal solution?
2. Give (a) two examples of exothermic mixing of two liquids and (b) two examples of endothermic mixing based on your experience.
3. Answer the following questions true or false:
 - a. Heat of mixing at infinite dilution involves mixing of 1 mole solute and an infinite amount of solvent and is therefore not defined.
 - b. Heats of reaction and mixing are approximately equal because they both involve molecular rearrangement.
 - c. Ethyl alcohol and water form an ideal solution.
4. What are some of the significant differences between the H - x chart in Figure 28.3 and the integral heat of solution chart in Figure 28.2?

Problems

1. Use the heat of solution data in Appendix H to determine the heat transferred per mole of entering solution into or out of (state which) a process in which 2 g mol of a 50 mole % solution of sulfuric acid at 25°C is mixed with water at 25°C to produce a solution at 25°C containing a mole ratio of 10 H₂O to 1 H₂SO₄.
2. Calculate the heat that must be added or removed per ton of 50 wt % H₂SO₄ produced by the process shown in Figure SAT28.2P2.

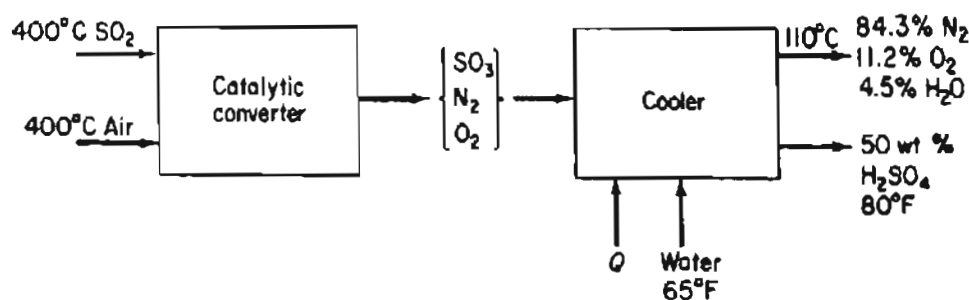


Figure SAT28.2P2

3. For the sulfuric acid-water system, what are the phase(s), composition(s), and enthalpy(ies) existing at $\Delta \hat{H} = 120$ Btu/lb and $T = 260^\circ\text{F}$?
4. Estimate the heat of vaporization of an ethanol-water mixture at 1 atm and an ethanol mass fraction of 0.50 from the enthalpy-concentration chart in Appendix I.

Thought Problem

1. An example of an accident occurred in a tank as shown in Figure TP28.2-1. A problem occurred in discharging the NaOH (caustic) solution by air pressure because the end of the dip pipe was broken. The manhole cover was removed, and a scraper rod was lowered into the liquid to remove the broken part of the dip pipe. An immediate explosion occurred that shot NaOH solution 30 feet into the air, killing one man. What was the cause of the explosion?

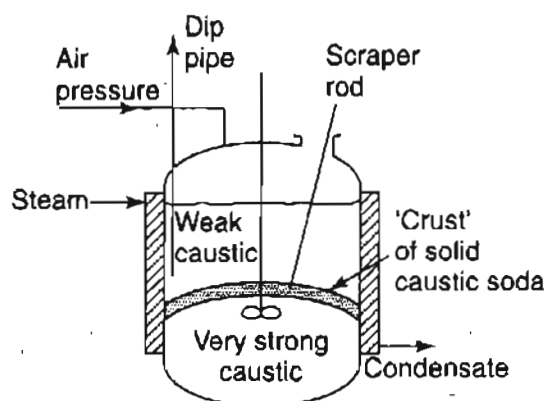


Figure TP28.2-1

Looking Back

In this chapter we described how to carry out energy balances when enthalpy changes occur because of the heat of solution or mixing. We also described how to use binary enthalpy-concentration charts.

GLOSSARY OF NEW WORDS

Enthalpy-concentration diagram A convenient graphical way to represent enthalpy data for binary solutions that features a plot of specific enthalpy versus concentration (usually mass or mole fraction) with temperature as a parameter.

Heat of solution at infinite dilution The asymptotic value of the heat of solution of 1 mole of solute dissolved in an infinite amount of solvent.

Heat (enthalpy) of dissolution The negative of the heat of solution or mixing.

Heat (enthalpy) of mixing The enthalpy change that occurs when a liquid is mixed with a liquid.

Heat (enthalpy) of solution The enthalpy change that occurs when a solute is mixed with a solvent.

Ideal solution A solution comprised of several components in which a property is the weighted sum of the properties of the individual components.

Incremental (differential) heat of solution The derivative of the integral heat of solution curve.

Integral heat of solution The heat of solution for the combination of 1 mole of solute with n moles of solvent.

Real solution Nonideal solution.

Solute The compound that is dissolved in a solvent.

Solvent The compound in which the solute is dissolved.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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Web Sites

http://www.encyclopedia.com/html/section/solution_HeatofSolution.asp

<http://www.factmonster.com/ce6/sci/A0861176.html>

<http://newton.dep.anl.gov/askasci/chem99/chem99198.htm>

<http://www.onlink.net/~bernas/heatsolution.htm>

PROBLEMS

- *28.1** If the heat of formation of LiCl (s) is $-408.78 \text{ kJ/kg LiCl}$, calculate the heat of formation of LiCl in 10 moles of water. The heat of solution is $-32.84 \text{ kJ/kg LiCl}$.
- **28.2** Home ice cream makers use a mixture of 3 parts of ice to 1 part of salt (NaCl) to freeze the ice cream. Why does this process work?

Based on the following data, is salt the best compound to use (with the amount of water shown) for a freezing mixture?

Compound	$\Delta \hat{H}_f^\circ (\text{kJ/g mol})$
$\text{H}_2\text{O (s)}$	-290.852
(l)	-285.840
(g)	-241.826
NaCl(s)	-411.00
$\text{NaCl [10 H}_2\text{O]}$	-408.99
$\text{NH}_4\text{Cl (s)}$	-315.43
$\text{NH}_4\text{Cl [10 H}_2\text{O]}$	-301.33
$\text{CaCl}_2 \text{ (s)}$	-794.97
$\text{CaCl}_2 \text{ [10 H}_2\text{O]}$	-860.03
$\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$	-2586.5
$\text{CaCl}_2 \text{ [6 H}_2\text{O]}$	-854.4

- **28.3** Based on the following data for the solution of Na_2CO_3 at SC:

Compound	$\Delta \hat{H}_f^\circ (\text{kJ/g mol})$
$\text{Na}_2\text{CO}_3 \text{ (s)}$	-1130.92
in 15 mol H_2O	-1163.70
20	-1162.78
25	-1161.98
40	-1160.72
75	-1158.01
100	-1157.17
200	-1155.50
400	-1154.39
$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O (s)}$	-1430.09
$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O (s)}$	-3201.18
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O (s)}$	-4081.9

(a) draw a standard integral heat of solution curve for sodium carbonate dissolved in water showing the heat of solution in kJ per mole of sodium carbonate vs. mole of water; (b) if 143 kg of sodium carbonate is added to 180 kg of water, what would be the approximate final temperature of the solution if the mixing were adiabatic?

- **28.4** (a) From the data below, plot the enthalpy of 1 mole of solution at 27°C as a function of the weight percent HNO_3 . Use as reference states liquid water at 0°C and liquid

HNO_3 at 0°C . You can assume that C_p for H_2O is $75 \text{ J}/(\text{g mol})(^\circ\text{C})$ and for HNO_3 , $125 \text{ J}/(\text{g mol})(^\circ\text{C})$.

$-\Delta H_{\text{soln}}$ at 27°C (J/g mol HNO_3)	Moles H_2O added to 1 g mol HNO_3
0	0.0
3,350	0.1
5,440	0.2
6,900	0.3
8,370	0.5
10,880	0.67
14,230	1.0
17,150	1.5
20,290	2.0
24,060	3.0
25,940	4.0
27,820	5.0
30,540	10.0
31,170	20.0

(b) Compute the energy absorbed or evolved at 27°C on making a solution of 4 moles of HNO_3 and 4 moles of water by mixing a solution of $33 \frac{1}{3} \text{ mol } \%$ acid with one of $60 \text{ mol } \%$ acid.

****28.5** *National Bureau of Standards Circular 500* gives the following data for calcium chloride (mol. wt. 111) and water:

Formula	State	$-\Delta H_f$ at 25°C (kcal/g mol)
H_2O	Liquid	68.317
	Gas	57.798
CaCl_2	Crystal	190.0
	in 25 moles of H_2O	208.51
	50	208.86
	100	209.06
	200	209.20
	500	209.30
	1000	209.41
	5000	209.60
	∞	209.82
$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	Crystal	265.1
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	Crystal	335.5
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$	Crystal	480.2
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	Crystal	623.15

Calculate the following:

- (a) The energy evolved when 1 lb mol of CaCl_2 is made into a 20% solution at 77°F ;
- (b) The heat of hydration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to the hexahydrate;
- (c) The energy evolved when a 20% solution containing 1 lb mol of CaCl_2 is diluted with water to 5% at 77°F .

***28.6** For each of the following processes that occur in an open steady state system, calculate the heat transfer to or from the system if it is isothermal.

- (a) 1000 g of O_2 are mixed with 1000 g of CO_2 .
- (b) 900 kg of water are mixed with 63 kg of nitric acid.

Data at SC:

Compound	\hat{H}_f° (kJ/kg)
HNO_3 (liquid)	-173.234
In 1 g mol H_2O	-186.347
2 H_2O	-193.318
5 H_2O	-201.962
10 H_2O	-205.014
50 H_2O	-205.978
100 H_2O	-205.983

****28.7** An insulated closed tank contains 250 kg of a 20% solution of sulfuric acid at its boiling point. One hundred pounds of a 98% solution of sulfuric acid is carefully added to the original solution with stirring. What is the final temperature, composition, and weight of solution in the tank? Use Appendix I.

***28.8** An insulated tank contains 500 kg of a solution of 20% sulfuric acid at 340 K. To this solution is added 300 kg of a 96% solution of sulfuric acid at 310 K. To heat the solution, 100 kg of superheated steam are introduced at 1 atm and 400 K. What is the final temperature in the solution, and what are the concentrations of sulfuric acid and water in the final solution?

****28.9** A vessel contains 100 g of an $\text{NH}_4\text{OH}-\text{H}_2\text{O}$ liquid mixture at 1 atm that is 15.0% by weight NH_4OH . Just enough aqueous H_2SO_4 is added to the vessel from an H_2SO_4 liquid mixture at 25°C and 1 atm (25.0 mole % H_2SO_4) so that the reaction to $(\text{NH}_4)_2\text{SO}_4$ is complete. After the reaction, the products are at 25°C and 1 atm. How much heat (in J) is absorbed or evolved by this process? It may be assumed that the final volume of the products is equal to the sum of the volumes of the two initial mixtures.

*****28.10** An ammonium hydroxide solution is to be prepared at 77°F by dissolving gaseous NH_3 in water. Prepare charts showing:

- (a) The amount of cooling needed (in Btu) to prepare a solution containing 1 lb mol of NH_3 at any concentration desired;
- (b) The amount of cooling needed (in Btu) to prepare 100 gal of a solution of any concentration up to 35% NH_3 ;
- (c) If a 10.5% NH_3 solution is made up without cooling, at what temperature will the solution be after mixing?

- *28.11** An evaporator at atmospheric pressure is designed to concentrate 10,000 lb/hr of a 10% NaOH solution at 70°F into a 40% solution. The steam pressure inside the steam chest is 40 psig. Determine the pounds of steam needed per hour if the exit strong caustic preheats the entering weak caustic in a heat exchanger, leaving the heat exchanger at 100°F.
- **28.12** A 50% by weight sulfuric acid solution is to be made by mixing the following:
- (a) Ice at 32°F
 - (b) 80% H_2SO_4 at 100°F
 - (c) 20% H_2SO_4 at 100°F
- How much of each must be added to make 1000 lb of the 50% solution with a final temperature of 100°F if the mixing is adiabatic?
- *28.13** Saturated steam at 300°F is blown continuously into a tank of 30% H_2SO_4 at 70°F. What is the highest concentration of liquid H_2SO_4 that can result from this process?
- **28.14** One thousand pounds of 10% NaOH solution at 100°F is to be fortified to 30% NaOH by adding 73% NaOH at 200°F. How much 73% solution must be used? How much cooling must be provided so that the final temperature will be 70°F?
- 28.15*** A mixture of ammonia and water in the vapor phase, saturated at 250 psia and containing 80% by weight ammonia, is passed through a condenser at a rate of 10,000 lb/hr. Heat is removed from the mixture at the rate of 5,800,000 Btu/hr while the mixture passes through a cooler. The mixture is then expanded to a pressure of 100 psia and passes into a separator. A flow sheet of the process is given Fig. P28.15. If the heat loss from the equipment to the surroundings is neglected, determine the composition of the liquid leaving the separator by material and energy balances.

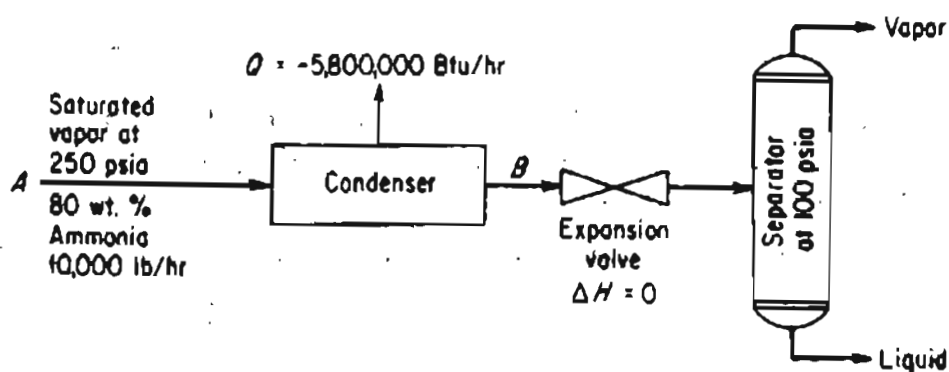


Figure P28.15

CHAPTER 29

HUMIDITY (PSYCHROMETRIC) CHARTS AND THEIR USE

29.1 Terminology	885
29.2 The Humidity (Psychrometric) Chart	888
29.3 Applications of the Humidity Chart	897

Your objectives in studying this chapter are to be able to:

1. Define and understand humidity, dry-bulb temperature, wet-bulb temperature, humidity chart, moist volume, and adiabatic cooling line.
2. Use the humidity chart to determine the properties of moist air.
3. Calculate enthalpy changes, and solve heating and cooling problems involving moist air.

In Chapter 18 we discussed humidity, dewpoint, relative humidity, and other properties of air–water mixtures. But we did not involve any energy effects, effects that are of considerable economic consequence. You have to be knowledgeable with the concepts involved in this chapter to complete your study of energy balances.

Looking Ahead

As you know, air is a mixture of various gases of constant composition plus water vapor in amounts that vary from time to time and place to place. What we will do in this chapter, after first presenting some new terminology, is discuss how to apply simultaneous material and energy balances to solve problems involving air and water, such as humidification, air conditioning, water cooling, and the like.

29.1 Terminology

Before proceeding with the discussion of the new terminology, you should first review some of the concepts treated in previous chapters. Look at Table 29.1 for a list of the main variables from previous chapters involved in this chapter.

Also recall that the humidity \mathcal{H} (*specific humidity*) is the mass (in lb or kg) of water vapor per unit mass (in lb or kg) of bone-dry air (some texts use moles of water vapor per mole of dry air as the humidity)

$$\mathcal{H} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{dry air}}} = \frac{18p_{\text{H}_2\text{O}}}{29(p_{\text{total}} - p_{\text{H}_2\text{O}})} = \frac{18n_{\text{H}_2\text{O}}}{29(n_{\text{total}} - n_{\text{H}_2\text{O}})} \quad (29.1)$$

Next let's introduce some related terminology for air–water vapor mixtures.

- a. The **humid heat** is the heat capacity of an air–water vapor mixture expressed on the basis of 1 lb or kg of bone-dry air. Thus the humid heat C_S is

$$C_S = C_{p \text{ air}} + (C_{p \text{ H}_2\text{O vapor}})(\mathcal{H}) \quad (29.2)$$

where the heat capacities are all energy per mass (and not per mole) per degree. Assuming that the heat capacities of air and water vapor are constant under the narrow range of conditions experienced for air-conditioning and humidification calculations, we can write in AE units

$$C_S = 0.240 + 0.45(\mathcal{H}) \quad \text{Btu}/(^{\circ}\text{F})(\text{lb dry air}) \quad (29.3a)$$

and in SI units,

$$C'_S = 1.00 + 1.88(\mathcal{H}) \quad \text{kJ}/(\text{K})(\text{kg dry air}) \quad (29.3b)$$

TABLE 29.1 Parameters Involved in Humidity Chart Calculations

Symbol	Meaning	SI value	AE value
$C_{p \text{ air}}$	Heat capacity of air	1.00 kJ/(kg)(K)	0.24 Btu/(lb)($^{\circ}\text{F}$)
$C_{p \text{ H}_2\text{O vapor}}$	Heat capacity of water vapor	1.88 kJ/(kg)(K)	0.45 Btu/(lb)($^{\circ}\text{F}$)
$\Delta \hat{H}_{\text{vap}}$	Specific heat of vaporization of water at 0 $^{\circ}\text{C}$ (32 $^{\circ}\text{F}$)	4502 kJ/kg	1076 Btu/lb
$\Delta \hat{H}_{\text{air}}$	Specific enthalpy of air	Equation (29.10)	Equation (29.9)
$\Delta \hat{H}_{\text{H}_2\text{O vapor}}$	Specific enthalpy of water vapor	steam tables	

- b. The **humid volume** is the volume of 1 lb or kg of dry air plus the water vapor in the air. In the AE system,

$$\begin{aligned}\hat{V} &= \frac{359 \text{ ft}^3}{1 \text{ lb mol}} \left| \frac{1 \text{ lb mol air}}{29 \text{ lb air}} \right| \frac{T_{\circ\text{F}} + 460}{32 + 460} \\ &+ \frac{359 \text{ ft}^3}{1 \text{ lb mol}} \left| \frac{1 \text{ lb mol H}_2\text{O}}{18 \text{ lb H}_2\text{O}} \right| \frac{T_{\circ\text{F}} + 460}{32 + 460} \left| \frac{\mathcal{H} \text{ lb H}_2\text{O}}{\text{lb air}} \right| \\ &= (0.730 T_{\circ\text{F}} + 336) \left(\frac{1}{29} + \frac{\mathcal{H}}{18} \right)\end{aligned}\quad (29.4)$$

where \hat{V} is in ft^3/lb dry air. In the SI system,

$$\begin{aligned}\hat{V}' &= \frac{22.415 \text{ m}^3}{1 \text{ kg mol}} \left| \frac{1 \text{ kg mol air}}{29 \text{ kg air}} \right| \frac{T_{\text{K}}}{273} \\ &+ \frac{22.415 \text{ m}^3}{1 \text{ kg mol}} \left| \frac{1 \text{ kg mol H}_2\text{O}}{18 \text{ kg H}_2\text{O}} \right| \frac{T_{\text{K}}}{273} \left| \frac{\mathcal{H} \text{ kg H}_2\text{O}}{\text{kg air}} \right| \\ &= 2.80 \times 10^{-3} T_{\text{K}} + 4.56 \times 10^{-3} T_{\text{K}} \mathcal{H}\end{aligned}\quad (29.5)$$

where \hat{V}' is in m^3/kg dry air.

- c. The **dry-bulb temperature** (T_{DB}) is the ordinary temperature you always have been using for a gas in $^{\circ}\text{F}$ or $^{\circ}\text{C}$ (or $^{\circ}\text{R}$ or K).
- d. The **wet-bulb temperature** (T_{WB}) is something new. As you may guess, even though you may never have heard of this term before, it has something to do with water (or other liquid, if we are concerned not with humidity but with saturation) evaporating from around an ordinary mercury thermometer bulb. Suppose that you put a wick, or porous cotton cloth, on the mercury bulb of a thermometer and wet the wick. Next you either (1) whirl the thermometer in the air as in Figure 29.1 (this apparatus is called a sling psychrometer when a wet-bulb and a dry-bulb thermometer are both mounted together), or (2) set up a fan to blow rapidly on the bulb at a high linear velocity. What happens to the temperature recorded by the wet-bulb thermometer?

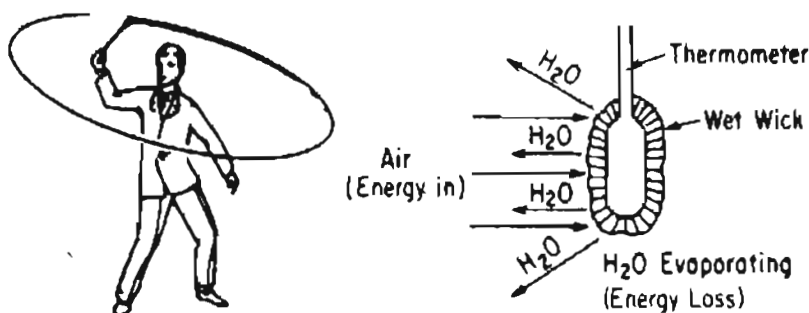


Figure 29.1 Web-bulb temperature obtained with a sling psychrometer.

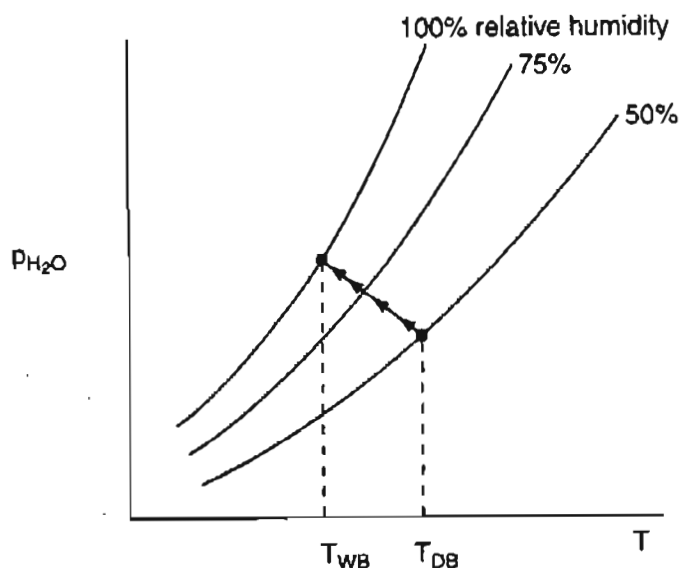


Figure 29.2 Evaporative cooling of the wick initially at T_{DB} causes a wicked thermometer at equilibrium to reach the wet-bulb temperature, T_{WB} .

As the water from the wick evaporates, the wick cools down and continues to cool until the steady-state rate of energy transferred to the wick by the air blowing on it equals the steady-state rate of loss of energy caused by the water evaporating from the wick. We say that the temperature of the bulb when the water in the wet wick is at equilibrium with the water vapor in the air is the wet-bulb temperature. (Of course, if water continues to evaporate, it eventually will disappear, and the wick temperature will rise to the dry bulb temperature.) The equilibrium temperature for the process described above will lie on the 100% relative humidity curve (saturated-air curve). Look at Figure 29.2.

SELF-ASSESSMENT TEST

Questions

1. On a copy of the p - H chart for water, plot the locus of where (a) the dry-bulb temperatures can be located; and (b) where the wet-bulb temperatures can be located.
2. Would the dew point temperatures be the locus of the wet-bulb temperatures?
3. Can psychrometric charts exist for mixtures other than water-air?
4. What is the difference between the wet- and dry-bulb temperatures?
5. Can the wet-bulb temperature ever be higher than the dry-bulb temperature?

Problems

1. Apply the Gibbs phase rule to an air-water vapor mixture. How many degrees of freedom exist (for the intensive variables)? If the pressure on the mixture is fixed, how many degrees of freedom result?

2. Prepare a chart in which the vertical axis is the humidity (Equation (29.1)) in $\text{kg H}_2\text{O/kg}$ dry air), and the horizontal axis is the temperature (in $^{\circ}\text{C}$). On the chart plot the curve of 100% relative humidity for water.
3. At 126°F and a humidity of $0.010 \text{ lb H}_2\text{O/lb}$ dry air, what is the humid volume?
4. Calculate the enthalpy change of air that has a humidity of $0.015 \text{ kg H}_2\text{O/kg}$ dry air when heated from 30°C to 50°C in kJ/kg dry air.

29.2 The Humidity (Psychrometric) Chart

The **humidity chart**, more formally known as the **psychrometric chart**, relates the various parameters involved in making combined material and energy balances for moist air. In the Carrier chart, the type of chart we will discuss, the vertical axis (usually placed on the righthand side) is the (specific) humidity, and the horizontal axis is the dry-bulb temperature. Examine Figure 29.3. On this chart we want to construct several other lines and curves featuring different parameters.

We will start with two of the new concepts and relations you read about in Section 29.1.

Wet-Bulb Line (Equation)

The equation for the **wet-bulb lines** is based on a number of assumptions, a detailed discussion of which is beyond the scope of this book. Nevertheless, as mentioned in Section 29.1, the idea of the wet-bulb temperature is based on the equilibrium between the *rates* of energy transfer to the bulb and the evaporation of water. The fundamental idea is that a large amount of air is brought into contact with a little bit of water, and that presumably the evaporation of the water leaves the temperature

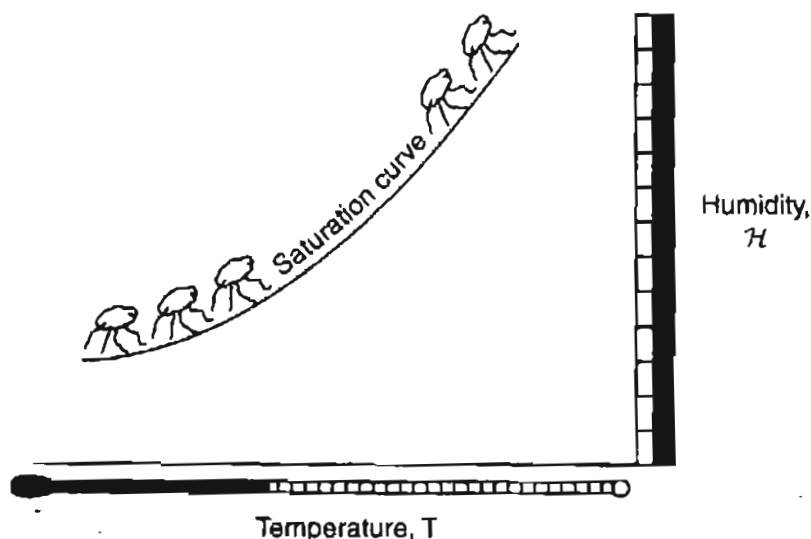


Figure 29.3 Major coordinates of the humidity chart.

and humidity of the air unchanged. Only the temperature of the water changes. The equation for the wet-bulb line evolves from an energy balance that equates the heat transfer to the water to the heat of vaporization of the water. Figure 29.4 shows several such lines on the psychrometric chart for air–water. The plot of \mathcal{H}_{WB} versus T_{WB} , the wet-bulb line, is approximately straight and has a negative slope.

What use is the wet-bulb line (equation)? You require two pieces of information to fix a state (point A in the humidity chart). One piece of information can be T_{DB} , \mathcal{H}_{DB} , \mathcal{RH} , and so on. The other can be T_{WB} . Where do you locate the value of T_{WB} on the humidity chart? The Carrier chart lists values of T_{WB} along the saturation curve (such as point B). You can also find the same values by projecting vertically upward from a temperature (point C) on the horizontal axis to the saturation curve (point B). If the process is a wet-bulb temperature process, all the possible states of the process fall on the wet-bulb line.

For example, for a known wet-bulb process, given an initial T_{DB} (along the horizontal axis) and \mathcal{H}_{DB} (along the vertical axis), the combination fixes a point on the graph (A). You can follow (up to the left) the wet-bulb process (line) to the saturation curve (B). Then project vertically downward onto the temperature axis to get the related T_{WB} (C), and project horizontally to the right to the related \mathcal{H}_{WB} (D). All points along the wet-bulb line are fixed by just one additional piece of information.

Adiabatic Cooling Line (Equation)

Another type of process of some importance occurs when **adiabatic cooling or humidification** takes place between air and water that is recycled, as illustrated in Figure 29.5. In this process the air is both cooled and humidified (its water content

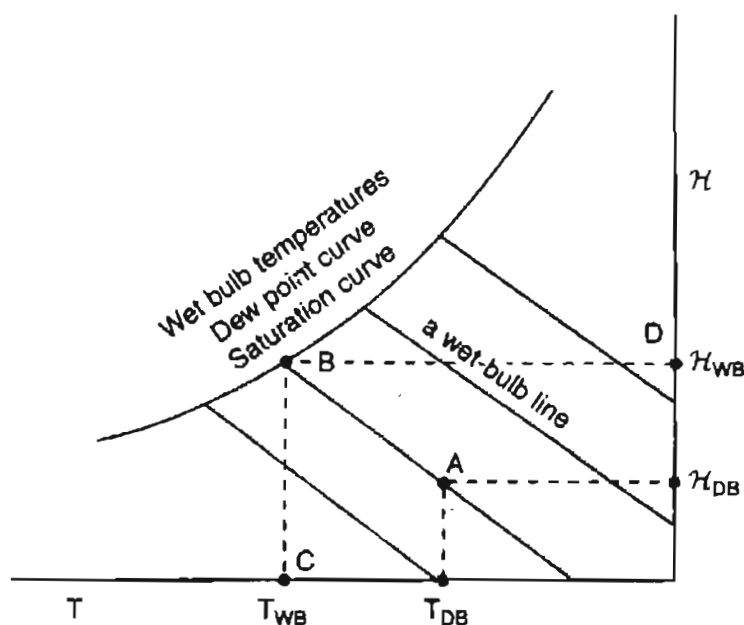


Figure 29.4 Representation of the wet-bulb process on an \mathcal{H} - T chart.

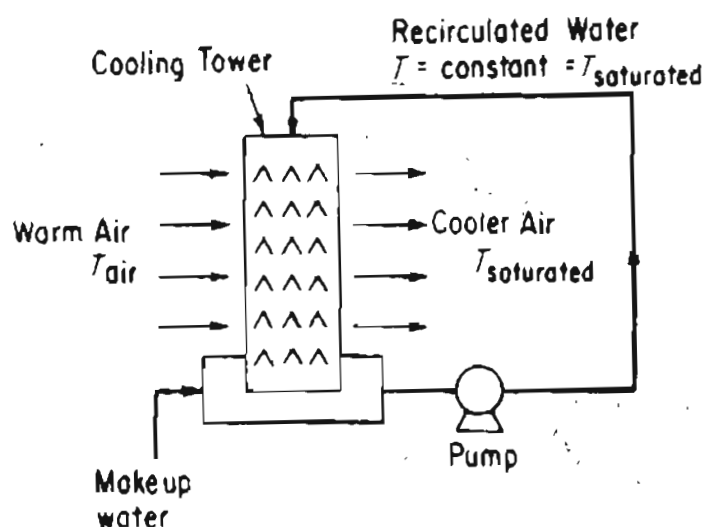


Figure 29.5 Adiabatic humidification with recycle of water.

risers) while a little bit of the recirculated water is evaporated. Thus, make-up water is added. At **equilibrium**, in the steady state, the temperature of the exit air is the same as the temperature of the water, and the exit air is saturated at this temperature. By making an overall energy balance around the process (with $Q = 0$), you can obtain the equation for the adiabatic cooling of the air.

It turns out that the wet-bulb process equation, *for water only*, is essentially the same relation as the adiabatic cooling equation. Thus, you have the nice feature that two processes can be represented by the same set of lines. The remarks we made above about locating parameters of moist air on the humidity chart for the wet-bulb process apply equally to the adiabatic humidification process. For a detailed discussion of the uniqueness of this coincidence, consult any of the references at the end of the chapter. For most other substances besides water, the respective equations will have different slopes.

In addition to the assumption that wet-bulb line is by coincidence identical to the adiabatic cooling line, let's look at some of the other details found on a humidity chart in which the vertical axis is \mathcal{H} and the horizontal axis is T . Look at Figure 29.6 and you will observe the following.

Lines and curves to particularly note are

1. Constant relative humidity indicated in percent.
2. Constant moist volume specific (humid volume).
3. Adiabatic cooling lines, which are the same (for water vapor only) as the wet-bulb or **psychrometric lines**.
4. The 100% relative humidity curve (i.e., saturated-air curve).
5. The specific enthalpy per mass of dry air (not air plus water vapor) for a saturated air–water vapor mixture:

$$\Delta \hat{H} = \Delta \hat{H}_{air} + \Delta \hat{H}_{H_2O \text{ vapor}}(\mathcal{H}) \quad (29.6)$$

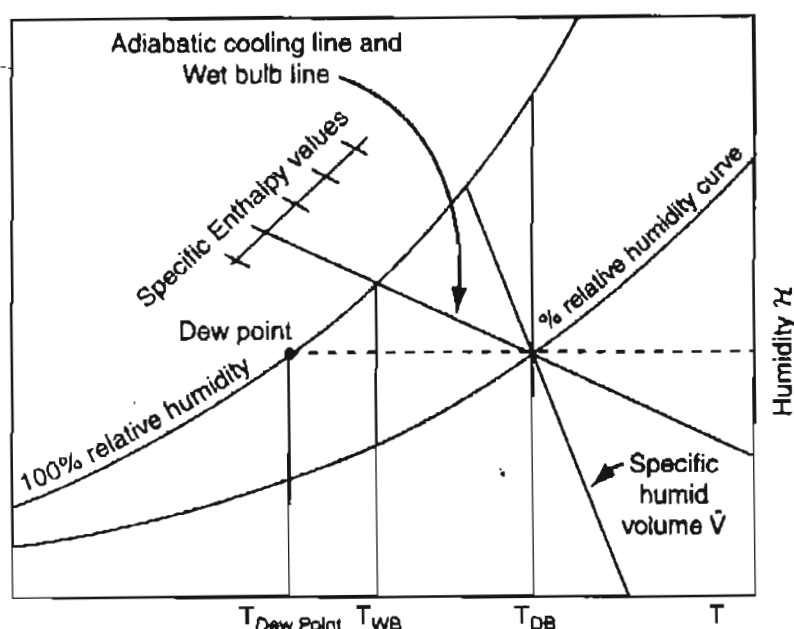


Figure 29.6 A skeleton humidity (psychrometric) chart showing typical relationships of the temperatures, dewpoint, wet- and dry-bulb temperatures, relative humidity, specific humid volume, humidity enthalpy, and adiabatic cooling/wet-bulb line.

Enthalpy adjustments for air less than saturated (identified by minus signs) are shown on the chart itself by a series of curves.

You can calculate the $\Delta \hat{H}$ values for the saturated air from equations or from tables that list the enthalpies of air and water vapor, or you can combine several of the equations discussed previously as follows.

$$\begin{aligned} \Delta \hat{H} = & C_{p,\text{air}}(T - T_{\text{ref}}) + \mathcal{H}[C_{p,\text{water vapor}}(T - T_S) + \Delta \hat{H}_{\text{vaporization at } T_S} \\ & + C_{p,\text{H}_2\text{O liquid}}(T_S - T_{\text{ref}})] \end{aligned} \quad (29.7)$$

Pick T_{ref} for H_2O as T_S , the saturation temperature of 32°F (0°C), so that the last term on the righthand side of Equation (29.7) is zero. Then

$$\Delta \hat{H} = C_{p,\text{air}}(T - T_{\text{ref}}) + \mathcal{H}C_{p,\text{water vapor}}(T - T_S) + \mathcal{H}\Delta H_{\text{vap at } T_S} \quad (29.8)$$

If you introduce Equation (29.2) into Equation (29.8), and select T_{ref} for air to be 0°F , in the AE system Equation (29.8) becomes

$$\Delta \hat{H} = (0.240 + 0.45 \mathcal{H})T_{\circ\text{F}} + 1075.2 \mathcal{H} \text{ in Btu/lb} \quad (29.9)$$

In the SI system with the reference temperature for air 0°C

$$\Delta \hat{H}' = (1.00 + 1.88 \mathcal{H})T_{\circ\text{C}} + 2501 \mathcal{H} \text{ in kJ/kg} \quad (29.10)$$

Figures 29.7a and 29.7b are reproductions of the Carrier psychrometric charts.

If you analyze the degrees of freedom for the intensive variables via the phase rule, you find

$$\mathcal{F} = 2 - \mathcal{P} + C = 2 - 1 + 2 = 3$$

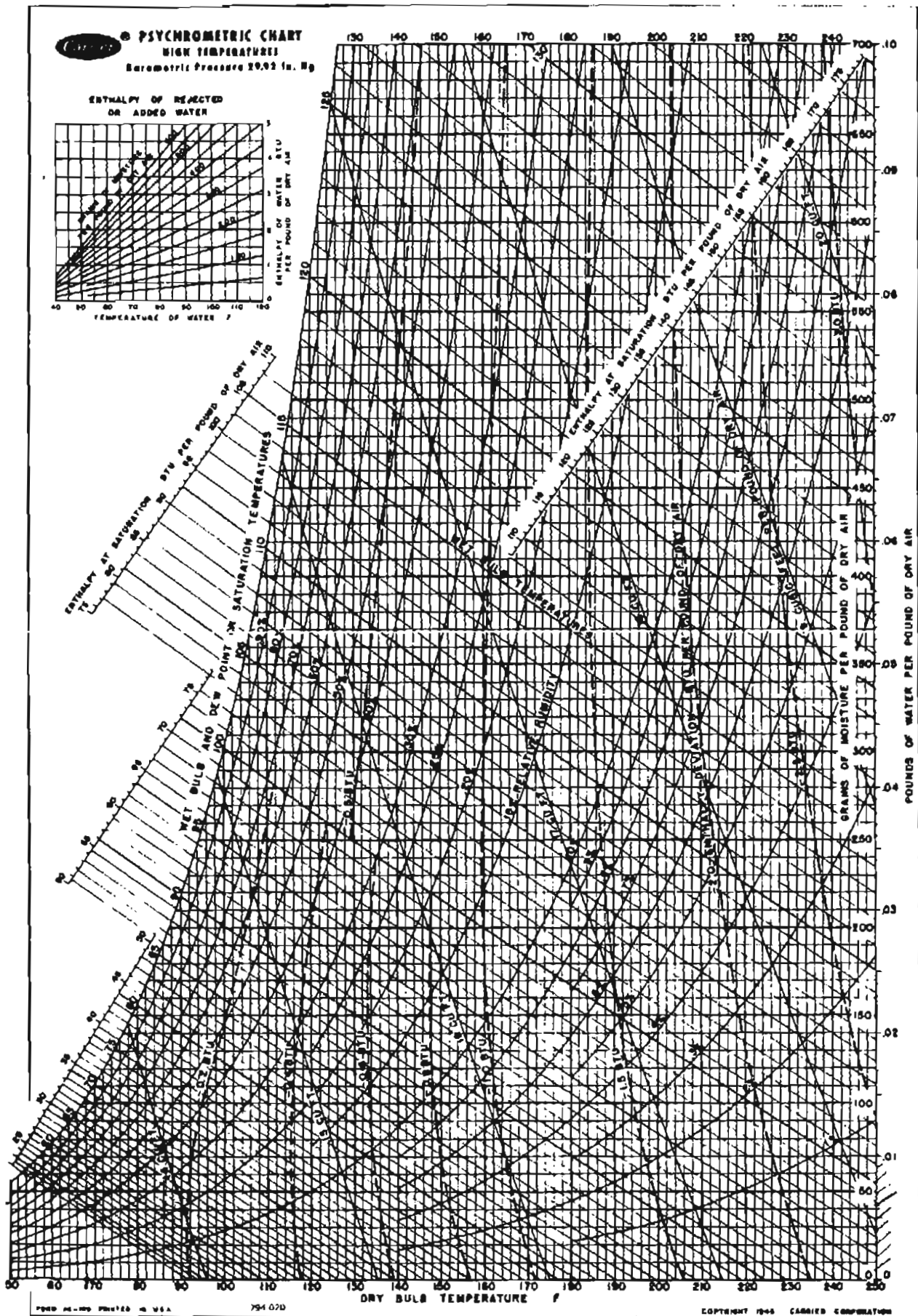


Figure 29.7a Psychrometric chart in AE units. (Reprinted by permission of Carrier Corporation)

Is this a paradox in view of our previous remarks stating that only two parameters are required to fix a point on the humidity chart? No.

A presumption for the chart is that the *pressure is fixed* at 1 atm. Consequently, $\mathcal{F} = 2$, and specification of any two values of the various variables shown on the chart, fix a specific point. Values for all of the other variables are correspondingly fixed.

The adiabatic cooling lines are lines of almost constant enthalpy for the entering air–water mixture, and you can use them as such without much error (1 or 2%). Follow the line on the chart up to the left to where the values for the enthalpies of saturated air appear. If you want to correct a saturated enthalpy value for the deviation that exists for a less-than-saturated air–water vapor mixture, you can employ the enthalpy deviation lines, which appear on the chart, and can be used as illustrated in the examples below.

You can analyze any process that is not a wet-bulb process or an adiabatic process with recirculated water using the usual material and energy balances, taking the basic data for the calculations from the humidity charts (or equations). If there is any increase or decrease in the moisture content of the air in a psychrometric process, the small enthalpy effect of the moisture added to the air or lost by the air may be included in the energy balance for the process to make it more exact, as illustrated in the examples below.

Tables of the properties shown in the humidity charts exist if you need better accuracy than can be obtained via the charts, and computer programs, which you can find on the Internet, can be used to retrieve psychrometric data. Although we have been discussing humidity charts exclusively, charts can be prepared for mixtures of any two substances in the vapor phase, such as CCl_4 and air or acetone and nitrogen.

Now let's look at an example of getting data from the humidity chart. On the CD in the back of this book you will find an animated example of using the humidity chart to get data.

EXAMPLE 29.1 Determining Properties of Moist Air from the Humidity Chart

List all of the properties you can find on the humidity chart in AE units for moist air at a dry-bulb temperature of 90°F and a wet-bulb temperature of 70°F. It is reasonable to assume that someone could measure the dry-bulb temperature using a typical mercury in glass thermometer and the wet-bulb temperature using a sling psychrometer.

Solution

A diagram will help explain the various properties that can be obtained from the humidity chart. See Figure E29.1.

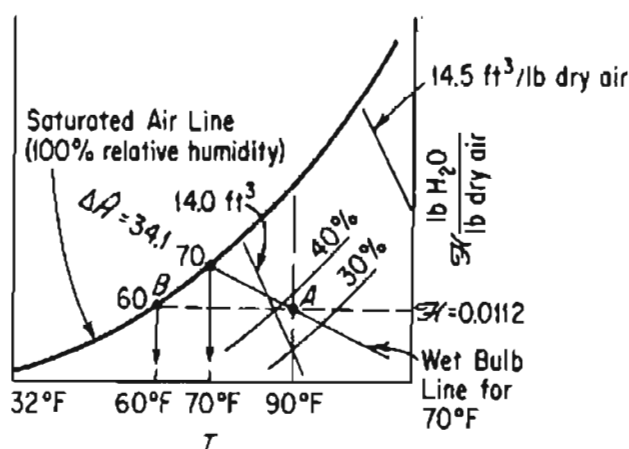


Figure E29.1

You can find the location of point A for 90°F DB (dry bulb) and 70°F WB (wet bulb) by following a vertical line from $T_{DB} = 90^\circ\text{F}$ until it crosses the wet-bulb line for 70°F. You can locate the end of a wet-bulb line by searching along the 100% humidity curve (saturation curve) until the label for the saturation temperature of 70°F is reached. Alternatively, you can proceed up a vertical line at 70°F until it intersects with the 100% humidity line.

Alternatively, from the wet-bulb temperature of 70°F follow the adiabatic cooling line (which is the same as the wet-bulb temperature line on the humidity chart) down to the right until it intersects the 90°F DB line. Now that point A has been fixed, you can read the other properties of the moist air from the chart.

- Dew point.** When the air at A is cooled at constant pressure (and in effect at constant humidity), as described in Chapter 17, it eventually reaches a temperature at which the moisture begins to condense. This process is represented by a horizontal line, a constant humidity line, on the humidity chart, and the dew point is located at B, or about 60°F.
- Relative humidity.** By interpolating between the 40% RH and 30% RH lines you can find that point A is at about 37% RH.
- Humidity (\mathcal{H}).** You can read the humidity from the righthand ordinate as 0.0112 lb H_2O /lb dry air.
- Humid volume.** By interpolation again between the 14.0 ft³/lb and the 14.5 ft³/lb lines, you can find the humid volume to be 14.1 ft³/lb dry air.
- Enthalpy.** The enthalpy value for saturated air with a wet-bulb temperature of 70°F is $\Delta H = 34.1$ Btu/lb dry air (a more accurate value can be obtained from psychrometric tables if needed). The enthalpy deviation shown by the dashed curves in Figure 29.7a (not shown in Figure E29.1) for less than saturated air is about -0.2 Btu/lb of dry air; consequently, the actual enthalpy of air at 37% RH is $34.0 - 0.2 = 33.8$ Btu/lb of dry air.

Frequently Asked Questions

- For what range of temperatures can a humidity chart be applied? Air conditioning applications range from about -10°C to 50°C . Outside this range of temperatures (and for other pressures), applications may require amended charts, tables, or calculations using equations.
- Can air and water vapor be treated as ideal gases in that range? Yes, with an error less than 0.2%.
- Will the enthalpy of the water vapor be a function of the temperature only? Yes, since the gas is assumed to be an ideal gas.
- How can you achieve greater accuracy than the values read from the humidity chart? Use the equations listed in Sections 29.1 and 29.2, or use a computer program.

SELF-ASSESSMENT TEST

Questions

1. What properties of an air–water vapor mixture are displayed on a humidity chart?
2. Explain what happens to both the air and water vapor when an adiabatic cooling process occurs.
3. Wet towels are to be dried in a laundry by blowing hot air over them. Can the Carrier humidity chart be used to help design the drier?
4. Can a humidity chart use values per mole rather than values per mass?

Problems

1. Air at a dry-bulb temperature of 200°F has a humidity of 0.20 mol H_2O /mol dry air. (a) What is its dew point? (b) If the air is cooled to 150°F , what is its dew point?
2. Air at a dry-bulb temperature of 71°C has a wet-bulb temperature of 52°C . (a) What is its percentage relative humidity? (b) If this air is passed through a washer-cooler, what would be the lowest temperature to which the air could be cooled without using refrigerated water?
3. Estimate for air at 70°C dry-bulb temperature, 1 atm, and 15% relative humidity: (a) kg H_2O /kg of dry air, (b) m^3/kg of dry air, (c) wet-bulb temperature (in $^{\circ}\text{C}$), (d) specific enthalpy, and (e) dew point (in $^{\circ}\text{C}$).
4. Calculate the following properties of moist air at 1 atm and compare with values read from the humidity chart.
 - (a) The humidity of saturated air at 120°F .
 - (b) The enthalpy of air in part (a) per pound of dry air.
 - (c) The volume per pound of dry air of the air in part (a).
 - (d) The humidity of air at 160°F with a wet-bulb temperature of 120°F .

Thought Problem

1. The use of home humidifiers has recently been promoted in advertisements as a means of providing more comfort in houses with the thermostat turned down. "Humidification makes life more comfortable and prolongs the life of furniture." Many advertisers describe a humidifier as an energy-saving device because it allows lower temperatures (4 or 5°F lower) with comfort. Is this true?

Discussion Problems

1. In cold weather, water vapor exhausted from cooling towers condenses and fog is formed as a plume. What are one or two *economically practical* methods of preventing such cooling?
2. In winter in the north, ice that forms at the intake of a rotating air-compressor can break off and be ingested by the compressor with resulting damage to the blades and internal parts. What can you recommend doing to prevent such accidents?

29.3 Applications of the Humidity Chart

Quite a few industrial processes exist for which you can involve the properties found on a humidity chart, including:

1. Drying—moist air enters and less moist air leaves the process.
2. Humidification—liquid water is vaporized into moist air.
3. Combustion—moist air enters a process and additional water is added to the moist air from the combustion products.
4. Air conditioning—moist air is heated and cooled.
5. Condensation—moist air is cooled below its saturation temperature.

EXAMPLE 29.2 Heating at Constant Humidity in a Home Furnace

Moist air at 38°C and 49% RH is heated in your home furnace to 86°C. How much heat has to be added per cubic meter of initial moist air, and what is the final dew point of the air?

Solution

As shown in Figure E29.2, the process has an input state at point A at $T_{DB} = 38^\circ\text{C}$ and 48% RH, and an output state at point B, which is located at the intersection of a horizontal line of constant humidity with the vertical line up from $T_{DB} = 86^\circ\text{C}$. The dew point is unchanged in this process because the humidity is unchanged, and is located at C at 24.8°C.

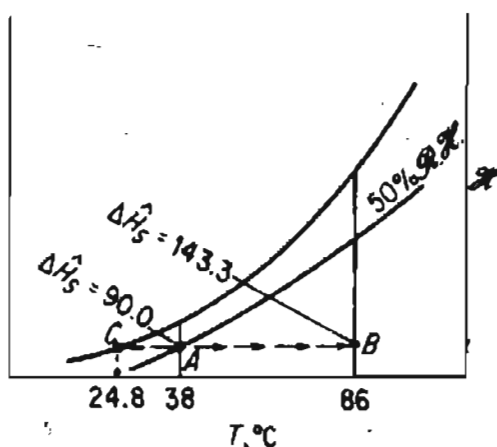


Figure E29.2

The enthalpy values are as follows (all in kJ/kg of dry air):

Point	$\Delta \hat{H}_{\text{satd}}$	δH	$\Delta \hat{H}_{\text{actual}}$
A	90.0	-0.5	89.5
B	143.3	-3.3	140.0

The value for the reduction of $\Delta \hat{H}_{\text{satd}}$ via δH is obtained from the enthalpy deviation lines (not shown in Figure E29.2) whose values are printed about one-fourth of the way down from the top of the chart. Also, at A the volume of the moist air is $0.91 \text{ m}^3/\text{kg}$ of dry air. Consequently, the heat added is (the energy balance reduces to $\hat{Q} = \Delta \hat{H}$): $140.0 - 89.5 = 50.5 \text{ kJ/kg}$ of dry air.

$$\frac{50.5 \text{ kJ}}{\text{kg dry air}} \left| \frac{1 \text{ kg dry air}}{0.91 \text{ m}^3} \right. = 55.5 \text{ kJ/m}^3 \text{ initial moist air}$$

EXAMPLE 29.3 Cooling and Humidification Using a Water Spray

One way of adding moisture to air is by passing it through water sprays or air washers. See Figure E29.3a. Normally, the water used is recirculated rather than wasted. Then, in the steady state, the water is at its adiabatic saturation temperature, which is the same as the wet-bulb temperature. The air passing through the washer is cooled, and if the contact time between the air and the water is long enough, the air will be at the wet-bulb temperature also.

However, we shall assume that the washer is small enough so that the air does not reach the wet-bulb temperature; instead, the following conditions prevail:

	$T_{\text{DB}}(^{\circ}\text{C})$	$T_{\text{WB}}(^{\circ}\text{C})$
Entering air	40	22
Exit air	27	

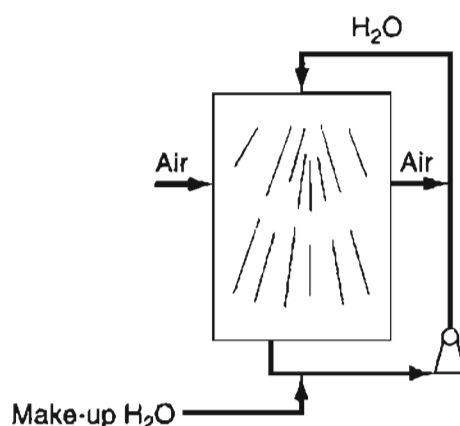


Figure 29.3a

Find the moisture added in kg per kilogram of dry air going through the humidifier.

Solution

The whole process is assumed to be *adiabatic*. As shown in Figure E29.3b, the process inlet conditions are at *A*. The outlet state is at *B*, which occurs at the intersection of the adiabatic cooling line (the same as the wet-bulb line) with the vertical line at $T_{DB} = 27^\circ\text{C}$. The wet-bulb temperature remains constant at 22°C . Humidity values are

	$\mathcal{H}\left(\frac{\text{kgH}_2\text{O}}{\text{kg dry air}}\right)$
<i>B</i>	0.0145
<i>A</i>	0.0093

Difference: $0.0052 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}} \text{ added}$

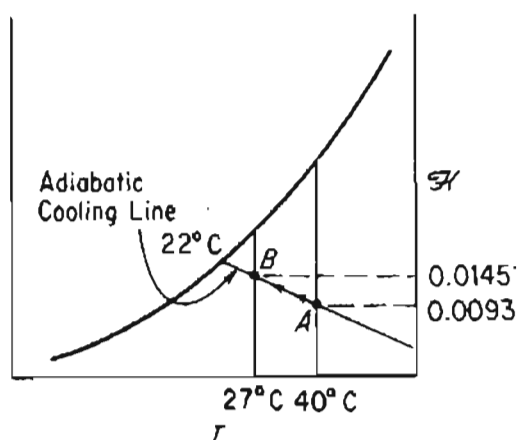


Figure E29.3b

EXAMPLE 29.4 Combined Material and Energy Balances for a Cooling Tower

You have been requested to redesign a water-cooling tower that has a blower with a capacity of $8.30 \times 10^6 \text{ ft}^3/\text{hr}$ of moist air. The moist air enters at 80°F and a wet-bulb temperature of 65°F . The exit air is to leave at 95°F and 90°F wet bulb. How much water can be cooled in pounds per hour if the water to be cooled enters the tower at 120°F , leaves the tower at 90°F , and is not recycled?

Solution

Figure E29.4 shows the process and the corresponding states on the humidity chart.

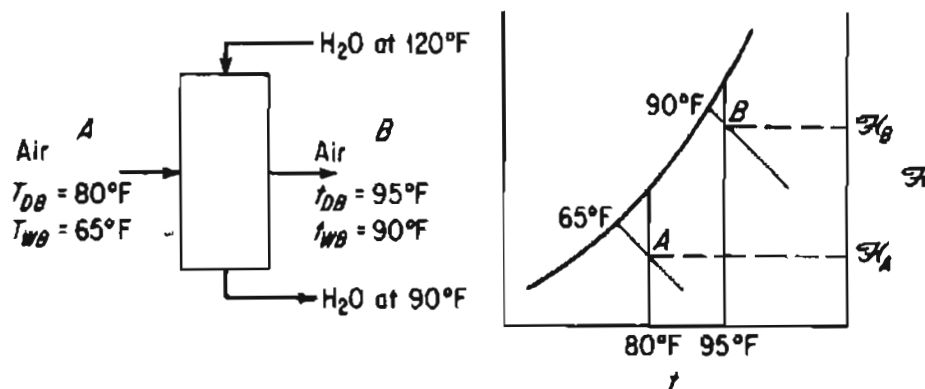


Figure E29.4

Enthalpy, humidity, and humid volume data for the air taken from the humidity chart are as follows:

	A	B
$\mathcal{H}\left(\frac{\text{lb H}_2\text{O}}{\text{lb dry air}}\right)$	0.0098	0.0297
$\mathcal{H}\left(\frac{\text{grains H}_2\text{O}}{\text{lb dry air}}\right)$	69	208
$\Delta\hat{H}\left(\frac{\text{Btu}}{\text{lb dry air}}\right)$	$30.05 - 0.12 = 29.93$	$55.93 - 0.10 = 55.83$
$\hat{V}\left(\frac{\text{ft}^3}{\text{lb dry air}}\right)$	13.82	14.65

The cooling-water exit rate can be obtained from an energy balance around the process.

Basis: $8.30 \times 10^6 \text{ ft}^3/\text{hr}$ of moist air $\equiv 1 \text{ hour}$

The entering air is

$$\frac{8.30 \times 10^6 \text{ ft}^3}{13.82 \text{ ft}^3} \left| \frac{1 \text{ lb dry air}}{13.82 \text{ ft}^3} \right| = 6.01 \times 10^5 \text{ lb dry air}$$

The relative enthalpy of the entering water stream per pound is (the reference temperature for the water stream is 32°F and 1 atm)

$$\Delta \hat{H} = C_{p\text{H}_2\text{O}} \Delta T = (120 - 32)(1) = 88 \text{ Btu/lb H}_2\text{O}$$

and that of the exit stream is $90 - 32 = 58 \text{ Btu/lb H}_2\text{O}$. (The value from the steam tables at 120°F for liquid water of 87.92 Btu/lb H₂O is slightly different since it represents water at its vapor pressure [1.69 psia] based on reference conditions of 32°F and liquid water at its vapor pressure). Any other reference datum could be used instead of 32°F for the liquid water. For example, if you chose 90°F, one water stream would not have to be taken into account because its relative enthalpy would be zero. In any case, the enthalpies of the reference state will cancel when you calculate enthalpy differences.

The transfer of water to the air is

$$0.0297 - 0.0098 = 0.0199 \text{ lb H}_2\text{O/lb dry air}$$

(a) *Material balance for the liquid water stream:*

Let $W = \text{lb H}_2\text{O}$ entering the tower in the water stream per lb dry air. Then

$$W - 0.0199 = \text{lb H}_2\text{O leaving tower in the water stream per lb dry air}$$

(b) *Material balance for the dry air:*

$$6.01 \times 10^5 \text{ lb in} = 6.01 \times 10^5 \text{ lb dry air out}$$

(c) *Energy balance (enthalpy balance) around the entire process:*

Although the reference temperature for the moist air (0°F) is not the same as that for liquid water (32°F), the reference enthalpies cancel in the calculations, as mentioned above.

Air and water in air entering		Water stream entering
$\frac{29.93 \text{ Btu}}{1 \text{ lb dry air}} \left \frac{6.01 \times 10^5 \text{ lb dry air}}{13.82 \text{ ft}^3} \right $	+	$\frac{88 \text{ Btu}}{1 \text{ lb H}_2\text{O}} \left \frac{W \text{ lb H}_2\text{O}}{1 \text{ lb dry air}} \right \frac{6.01 \times 10^5 \text{ lb dry air}}{13.82 \text{ ft}^3}$

Air and water in air leaving

$$= \frac{55.83 \text{ Btu}}{1 \text{ lb dry air}} \left| \frac{6.01 \times 10^5 \text{ lb dry air}}{13.82 \text{ ft}^3} \right|$$

Water stream leaving

$$+ \frac{58 \text{ Btu}}{1 \text{ lb H}_2\text{O}} \left| \frac{(W - 0.0199) \text{ lb H}_2\text{O}}{1 \text{ lb dry air}} \right| \frac{6.01 \times 10^5 \text{ lb dry air}}{13.82 \text{ ft}^3}$$

$$29.93 + 88W = 55.83 + 58(W - 0.0199)$$

$$W = 0.825 \text{ lb H}_2\text{O/lb dry air}$$

$$W - 0.0199 = 0.805 \text{ lb H}_2\text{O/lb dry air}$$

The total water leaving the tower is

$$\frac{0.805 \text{ lb H}_2\text{O}}{\text{lb dry air}} \left| \frac{6.01 \times 10^5 \text{ lb dry air}}{\text{hr}} \right| = 4.85 \times 10^5 \text{ lb/hr}$$

EXAMPLE 29.5 Drying of Chlorella

A solution containing the cells of *Chlorella* is to be dried by evaporating 100 lb of water per hour in a dryer. After purification, the air to be used has a humidity of 0.020 lb H₂O/lb dry air and a temperature of 90°F. This air is preheated to a dry bulb temperature of 155°F before entering the dryer. The air leaving the dryer has a dry bulb temperature of 110°F and a wet bulb temperature of 100°F. Calculate the air consumption of the dryer in ft³/hr at 90°F and 1 atm.

Solution

Figure E29.5 for the process includes the data.

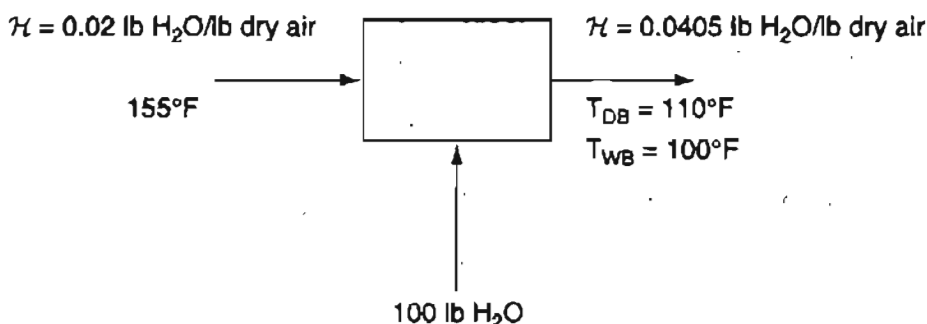


Figure E29.4

Basis: 1 hr (100 lb H₂O)

From the AE humidity chart at $T_{DB} = 110^\circ\text{F}$ and $T_{WB} = 100^\circ\text{F}$, $\mathcal{H} = 0.0405 \text{ lb H}_2\text{O/lb dry air}$ (placed on the diagram). The dry air is a tie element (the same amount of air that goes in that goes out) so that

$$\mathcal{H}_{\text{out}} - \mathcal{H}_{\text{in}} = 0.0405 - 0.0200 = 0.0205 \text{ lb H}_2\text{O/lb dry air}$$

$$\frac{100 \text{ lb H}_2\text{O evaporated}}{0.0205 \text{ lb H}_2\text{O}} \left| \frac{1 \text{ lb dry air}}{1.02 \text{ lb wet air}} \right| = 4980 \text{ lb wet air in}$$

Assume the molecular weight of the wet air is 29 (an insignificant error occurs). Then

$$\frac{4980 \text{ lb wet air}}{29 \text{ lb air}} \left| \frac{1 \text{ lb mol wet air}}{359 \text{ ft}^3} \right| \frac{460 + 90}{460 + 32} = 6.89 \times 10^4 \text{ ft}^3 \text{ at } 90^\circ\text{F and } 1 \text{ atm}$$

SELF-ASSESSMENT TEST

Questions

1. In combustion calculations with air in previous chapters you usually neglected the moisture in the air. Is this assumption reasonable?
2. Is the use of the humidity charts restricted to adiabatic cooling or wet-bulb processes?

Problems

1. A process that takes moisture out of the air by passing the air through water sprays sounds peculiar but is perfectly practical as long as the water temperature is below the dew point of the air. Equipment such as shown in Figure SAT29.3P1 would do the trick. If the entering air has a dew point of 70°F and is at 40% RH, how much heat has to be removed by the cooler, and how much water vapor is removed, if the exit air is at 56°F with a dew point of 54°F ?

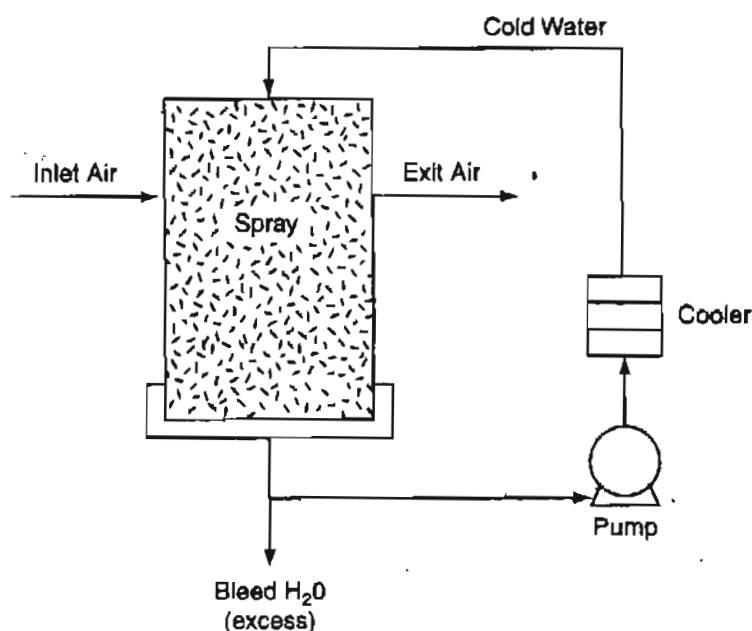


Figure SAT29.3P1

2. Humid air at 1 atm and 200°F, and containing 0.0645 lb of H_2O /lb of dry air, enters a cooler at the rate of 1000 lb of dry air per hour (plus accompanying water vapor). The air leaves the cooler at 100°F, saturated with water vapor (0.0434 lb of H_2O /lb of dry air). Thus 0.0211 lb H_2O is condensed per pound of dry air. How much heat is transferred to the cooler?

Thought Problems

1. Cooling systems known as "swamp coolers" are a low-cost, environment-friendly technology based on evaporative cooling—the natural evaporation of water, the same process that cools a sweating human body. In evaporative air-conditioning's simplest form, hot air is drawn through a water spray or through wet, porous pads. The exit air becomes cooler and more humid as it takes up water. The only moving parts requiring electrical power are a fan and a small water pump that moves the water to the top of the system. Will a swamp cooler be an effective cooler in a swamp?
2. In adiabatic operation of a cooling tower, make-up water has to be added to compensate for the water evaporated. As a result, a number of operating problems occur that would not occur without the vaporization of the water. What are some that you believe might occur?

Discussion Problem

1. In a small office building or a house, you have a choice between using central air-conditioning and window air-conditioners. List some of the factors that govern the use of one type of system versus the other, for example, under what circumstances are window units preferred to central air-conditioning?

Looking Back

In this chapter we described the structure of and information obtained from humidity charts, and showed how they can be used in material and energy balance calculations.

GLOSSARY OF NEW WORDS

Dry-bulb temperature The usual temperature of a gas or liquid.

Humid heat The heat capacity of an air–water vapor mixture per mass of bone-dry air.

Humid volume The volume of air including the water vapor per mass of bone dry air.

Humidity chart See Psychrometric chart.

Psychrometric chart A chart showing the humidity versus temperature along with all of the other properties of moist air.

Psychrometric line See Wet bulb-line.

Wet-bulb line The representation on the humidity chart of the energy balance in which the heat transfer to water from the air is assumed to equal the enthalpy of vaporization of liquid water.

Wet-bulb temperature The temperature reached at equilibrium for the vaporization of a small amount of water into a large amount of air.

SUPPLEMENTARY REFERENCES

In addition to the references listed in the Frequently Asked Questions in the front material, the following are pertinent.

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Web Sites

<http://www-ceng.crna.fr/eng/software>

<http://www.chemicallogic.com>

<http://www.chempute.com/psychro.htm>

<http://eng.sdsu.edu/testcenter/Test/solv...ms/closed/process/specific/specific.html>

<http://www.handsdownsoftware.com>

http://www.linric.com/psyc_98.htm

<http://www.owl.net.rice.edu/~ceng301/42.html#4.2.1a>

<http://www.usatoday.com/weather/whumcalc.htm>

PROBLEMS

- *29.1** Autumn air in the deserts of the southwestern United States during the day will typically be moderately hot and dry. If a dry-bulb temperature of 27°C and a wet-bulb temperature of 17°C is measured for the air at noon: (a) What is the dew point? (b) What is the percent relative humidity? (c) What is the humidity?
- *29.2** Calculate:
- (a) The humidity of air saturated at 120°F
 - (b) The saturated volume at 120°F
 - (c) The humid heat.
- *29.3** Give expressions and/or definitions for the following:
- (a) saturated air
 - (b) percentage humidity
 - (c) humid heat
 - (d) humid volume
 - (e) saturated volume
 - (f) dew point
- **29.4** Urea is produced in cells as a product of protein metabolism. From the cells it flows through the circulatory system, is extracted in the kidneys, and excreted in the urine. In an experiment the urea was separated from the urine using ethyl alcohol, and dried in a stream of carbon dioxide. The gas analysis at 40°C and 100 kPa was 10% alcohol by volume and the rest carbon dioxide. Determine the following:
- a. The grams of alcohol per gram of CO_2 .
 - b. The percent relative saturation.
 - c. The humid heat.
 - d. The humid volume.
 - e. What the humid volume would be if the CO_2 were saturated with alcohol.
- *29.5** What is the difference between the constant enthalpy and constant wet bulb temperature lines on the humidity chart?
- *29.6** Under what conditions are the dry bulb, wet bulb, and dew point temperatures equal?
- *29.7** Explain how you locate the dew point on a humidity chart for a given state of moist air.
- *29.8** Under what conditions can the dry bulb and wet bulb temperatures be equal?
- *29.9** What does a home air conditioning unit do besides cooling the air in the house?
- *29.10** Under what conditions are the adiabatic saturation temperature and the wet bulb temperature the same?
- *29.11** Why is a process of just heating or cooling of moist air represented as a horizontal line on the humidity chart?
- *29.12** Moist air has a humidity of 0.020 kg of H_2O /kg of air. The humid volume is $0.90 \text{ m}^3/\text{kg}$ of air.
- (a) What is the dew point?
 - (b) What is the percent relative humidity?

- *29.13** Moist air at 100 kPa, a dry-bulb temperature of 90°C , and a wet-bulb temperature of 46°C is enclosed in a rigid container. The container and its contents are cooled to 43°C .
- What is the molar humidity of the cooled moist air?
 - What is the final total pressure in atm in the container?
 - What is the dew point in $^{\circ}\text{C}$ of the cooled moist air?
- *29.14** Use the humidity chart to estimate the kg of water vapor per kg of dry air when the dry bulb temperature is 30°C , and the relative humidity is 65%.
- *29.15** For air at an atmospheric pressure of 14.7 psia, a dry bulb temperature of 82°F , and a wet bulb temperature of 70°F , determine from the humidity chart:
- The humidity
 - The relative humidity
 - The vapor pressure of water at 82°F in psia and the pressure of the water vapor
 - The dew point
 - The enthalpy
 - The specific volume per pound of dry air
- *29.16** Humid air at 1 atm has a dry-bulb temperature of 180°F and a wet-bulb temperature of 120°F . The air is then cooled at 1 atm to a dry-bulb temperature of 115°F . Calculate the enthalpy change per lb of dry air.
- *29.17** What are the pounds of water vapor per pound of dry air when the dry bulb temperature is 80°F and the relative humidity is 65%.
- *29.18** What are the humidity, wet bulb temperature, humid volume, dew point, and specific enthalpy of air at 35°C and a relative humidity of 30%.
- *29.19** What are the relative humidity and specific enthalpy of air that has a dry bulb temperature of 40°C and a wet bulb temperature of 25°C .
- *29.20** What are the dry bulb temperature, wet bulb temperature, relative humidity humid volume, and enthalpy of air that has an absolute humidity of 0.02 kg/kg dry air and an enthalpy at saturation of 85.1 kJ/kg dry air.
- **29.21** The air supply for a dryer has a dry-bulb temperature of 32°C and a wet-bulb temperature of 25.5°C . It is heated to 90°C by coils and blown into the dryer. In the dryer, it cools along an adiabatic cooling line as it picks up moisture from the dehydrating material and leaves the dryer fully saturated.
- What is the dew point of the initial air?
 - What is its humidity?
 - What is its percent relative humidity?
 - How much heat is needed to heat 100 m^3 of initial air to 90°C ?
 - How much water will be evaporated per 100 m^3 of air entering the dryer?
 - At what temperature does the air leave the dryer?
- **29.22** Calculate:
- The humidity of air saturated at 120°F
 - The saturated volume at 120°F
 - The adiabatic saturation temperature and wet-bulb temperature of air having a dry-bulb $T = 120^{\circ}\text{F}$ and a dew point = 60°F

- (d) The percent saturation when the air in (c) is cooled to 82°F
- (e) The pounds of water condensed/100 lb of moist air in (c) when the air is cooled to 40°F
- *29.23 What is the lowest temperature that air can attain in an evaporative cooler if it enters at 1 atm, 29°C, and 40 percent relative humidity?
- *29.24 In heating and cooling systems, why is heated air sometimes humidified?
- *29.25 Why is cooled air in an air conditioning system sometimes reheated before discharging the air into a building?
- *29.26 On the humidity chart, does the adiabatic mixing of two airstreams yield a state for the mixture that has to be on the straight line connecting the states of the two streams?
- *29.27 A rotary dryer operating at atmospheric pressure dries 10 tons/day of wet grain at 70°F, from a moisture content of 10% to 1% moisture. The air flow is countercurrent to the flow of grain, enters at 225°F dry-bulb and 110°F wet-bulb temperature, and leaves at 125°F dry-bulb. See Fig. P29.27. Determine:
- The humidity of the entering and leaving air if the latter is saturated
 - The water removal in pounds per hour
 - The daily product output in pounds per day
 - The heat input to the dryer

Assume that there is no heat loss from the dryer, that the grain is discharged at 110°F, and that its specific heat is 0.18.

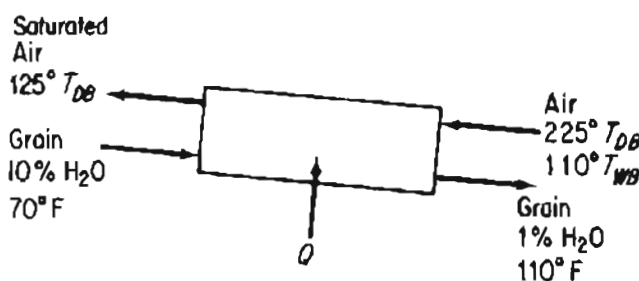


Figure P29.27

- *29.28 A stream of warm air with a dry-bulb temperature of 40°C and a wet-bulb temperature of 32°C is mixed adiabatically with a stream of saturated cool air at 18°C. The dry air mass flow rates of the warm and cool airstreams are 8 and 6 kg/s, respectively. Assuming a total pressure of 1 atm, determine (a) the temperature, (b) the specific humidity, and (c) the relative humidity of the mixture.
- *29.29 Temperatures (in °F) taken around a forced-draft cooling tower are as follows:

	In	Out
Air	85	90
Water	102	89

The wet-bulb temperature of the entering air is 77°F. Assuming that the air leaving the tower is saturated, calculate

- The humidity of the entering air
- The pounds of dry air through the tower per pound of water into the tower
- The percentage of water vaporized in passing through the tower.

- **29.30** A dryer produces 180 kg/hr of a product containing 8% water from a feed stream that contains 1.25 g of water per gram of dry material. The air enters the dryer at 100°C dry-bulb and a wet bulb temperature of 38°C; the exit air leaves at 53°C dry-bulb and 60% relative humidity. Part of the exit air is mixed with the fresh air supplied at 21°C, 52% relative humidity, as shown in Figure P29.30. Calculate the air and heat supplied to the heater, neglecting any heat lost by radiation, used in heating the conveyor trays, and so forth. The specific heat of the product is 0.18.

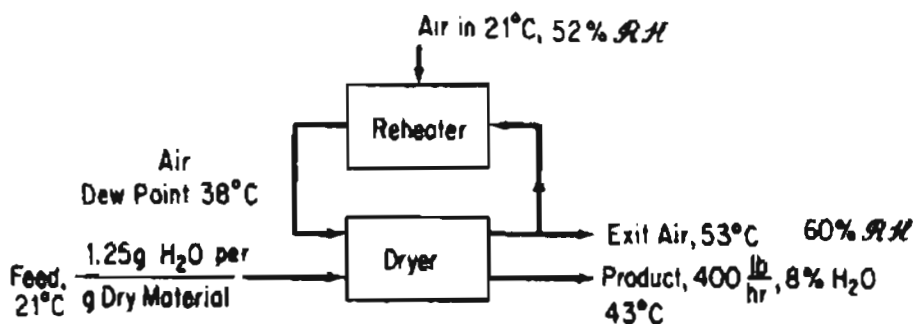


Figure P29.30

- **29.31** Air, dry-bulb 38°C, wet-bulb 27°C, is scrubbed with water to remove dust. The water is maintained at 24°C. Assume that the time of contact is sufficient to reach complete equilibrium between air and water. The air is then heated to 93°C by passing it over steam coils. It is then used in an adiabatic rotary drier from which it issues at 49°C. It may be assumed that the material to be dried enters and leaves at 46°C. The material loses 0.05 kg H₂O per kilogram of product. The total product is 1000 kg/hr.

- What is the humidity:
 - Of the initial air?
 - After the water sprays?
 - After reheating?
 - Leaving the drier?
- What is the percent humidity at each of the points in part (a)?
- What is the total weight of dry air used per hour?
- What is the total volume of air leaving the drier?
- What is the total amount of heat supplied to the cycle in joules per hour?

- **29.32** In the final stages of the industrial production of penicillin, air enters a dryer having a dry bulb temperature of 34°C and a wet bulb temperature of 17°C. The moist air flows over the penicillin at 1 atm at the rate of 4500 m³/hr. The air exits at 34°C. The penicillin feed enters at 34°C with a moisture content of 80%, and exits at 50%.

- How much water is evaporated from the penicillin per hour?
- What is the enthalpy change in kJ/hr of the air from inlet to exit?
- How many kg of the entering penicillin is dried per hour?

Assume that the properties of the wet penicillin are those of the water content of the mixture.

- *29.33** A person uses energy simply by breathing. For example, suppose that you breath in and out at the rate of 5.0 L/min, and that air with a relative humidity of 30% is inhaled at 25°C. You exhale at 37°C, saturated. What must be the heat transfer to the lungs from the blood system in kJ/hr to maintain these conditions? The barometer reads 97 kPa.
- **29.34** A plant has a waste product that is too wet to burn for disposal. To reduce the water content from 63.4% to 22.7%, it is passed through a rotary kiln drier. Prior to flowing through the kiln the air is first preheated in a heater by steam coils. To conserve energy, part of the exit gases from the kiln are recirculated and mixed with the heated air stream as they enter the kiln. An engineering intern stood by the entrance to the air heater, and measured a dry bulb temperature of 80°F and a wet bulb temperature of 54°F. She then moved to the exit of the kiln, and found that the dry bulb temperature was 120°F and the wet bulb temperature was 94°F. She next drew a sample of the moist air entering the kiln itself, and determined that the humidity was 0.0075 lb water per lb of dry air. Finally, she looked at the weather data on the TV, and saw that the barometer reading was 29.92 in. Hg.

Calculate:

- The percentage of the air leaving the kiln that is recirculated.
 - The lb inlet air per ton of dried waste.
 - The cubic feet of moist air leaving the kiln per ton of dried waste.
- **29.35** Air is used for cooling purposes in a plant process. The scheme shown in Fig. P29.35 has been proposed as a way to cool the air and continuously reuse it. In the process,

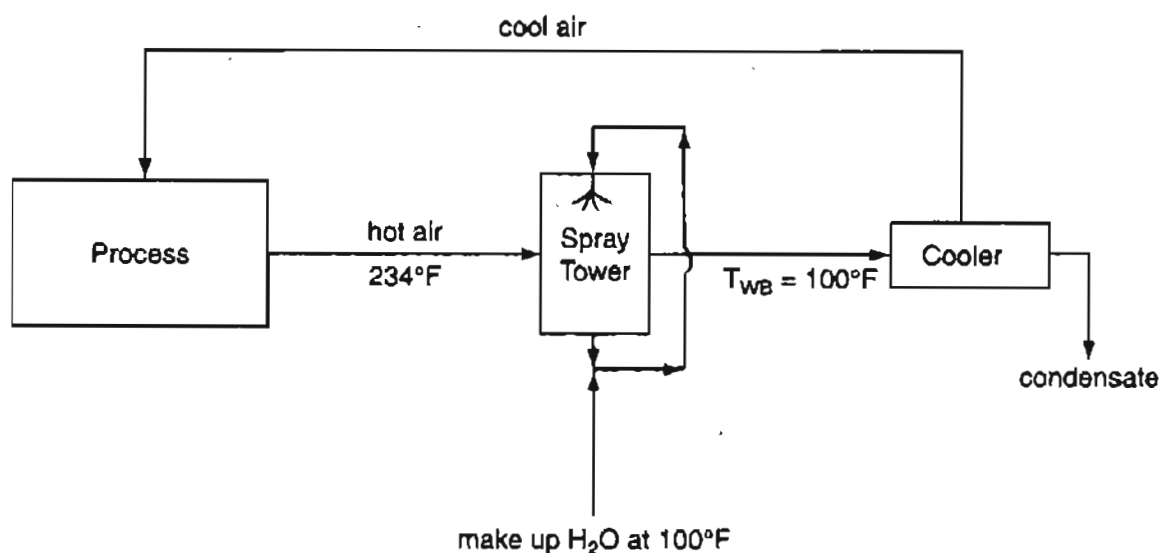


Figure P29.35

the air is heated and its water content remains constant. It is estimated that the air leaving the process will be at 234°F regardless of the entering temperature or the throughput rate. The air must remove 425,000 Btu/hr from the process.

Water for the spray tower is available at 100°F. This tower operates adiabatically with the air leaving saturated. Determine the following:

- a. the wet bulb temperature and per cent relative humidity of the air leaving the process,
- b. the temperature and dewpoint of the air leaving the cooler.
- c. sketch how this cycle would look on the psychrometric chart.
- d. the air circulation rate needed in lb BDA/hr.

CHAPTER 30

ANALYSIS OF THE DEGREES OF FREEDOM IN STEADY STATE PROCESSES

Now that you have accumulated some experience in making both material and energy balances, it is time to apply this knowledge to more complex problems. You have already encountered some simple examples of combined material and energy balances, as, for example, in the calculation of the adiabatic reaction temperature, where a material balance provides the groundwork for the implementation of an energy balance. An important aspect of solving complex problems is the determination that the degrees of freedom are indeed zero, that is, the problem is properly and completely specified.

Your objectives in studying this chapter are to be able to:

1. Identify the names and numbers of variables in the streams entering and leaving a processing unit, and the variables associated with the unit itself.
2. Determine the number of independent equations for each processing unit, the constraints.
3. Calculate the number of degrees of freedom (decision variables) for single units and combinations of units both without and with a reaction taking place.
4. Specify the values of variables equal to the number of degrees of freedom for a unit.

Looking Ahead

In this chapter we show how to calculate the degrees of freedom for a continuous steady-state process.

Main Concepts

An important aspect of combined material and energy balance problems is how to ensure that the process equations or sets of modules are determinate, that is, have at least one solution, and hopefully no more than one solution. The question is: How many variables are unknown, and consequently must have their values specified in any problem? The **number of degrees of freedom** is the number of variables in a set of independent equations to which values must be assigned so that the equations can be solved.

Let N_d = number of degrees of freedom, N_v = number of variables, and N_e = number of equations (material balances, restrictions, specifications, constraints). Then for N_e independent equations in general

$$N_d = N_v - N_e \quad (30.1)$$

and we conclude that $N_v - N_e$ variables must be specified **as long as the N_e equations are still independent**. You do not have to write down the equations during the analysis but just identify them. Whether the equations are linear or nonlinear makes no difference.

In this chapter the analysis of the degrees of freedom for a process assumes that the process is a steady-state flow process as commonly assumed in design. If operations or control is of interest, you would base the analysis on an unsteady process in which the accumulation term would be taken into consideration. (Also, not all of the variables in a process can be manipulated so the selection of which variables to specify is limited.)

Both extensive and intensive variables are included in the analysis in contrast with the degrees of freedom obtained from application of the phase rule in Chapter 19, which treats only intensive variables. What kinds of variables do you have to consider? Typical ones are

- (1) Temperature
- (2) Pressure
- (3) Either mass (mole) flow rate of each component in a stream, or the concentration of each component plus the total flow rate
- (4) Specific enthalpies (given in terms of temperature and pressure)
- (5) Heat flow, work (in the energy balance)
- (6) Recycle ratio

(7) Specifications

(8) Extent of reaction or fraction conversion

Some variables can be substituted for others, such as temperature and pressure for specific enthalpies, and stream flows for the recycle ratio.

Examine the flow stream in Figure 30.1. Two modes of specifying the number

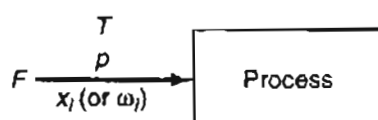


Figure 30.1 Stream variables

of variables associated with a process stream (**stream variables**) exist (we assume the stream is a single phase in which no reactions occur; with more than one phase, each phase would be treated as a separate stream):

Using moles (or mass) flow rate		Using compositions and total flow rate	
	No.		No.
Temperature (T)	1	Temperature (T)	1
Pressure (p)	1	Pressure (p)	1
Component flow rates (n_i or m_i)	N_{sp}	Compositions (x_i or ω_i)	$N_{sp} - 1$
		Total flow rate (F)	1
Total	$N_{sp} + 2$		$N_{sp} + 2$

where N_{sp} is the number of **components (species)** in the stream. The count for the number of compositions is $N_{sp} - 1$ and not N_{sp} because of the implicit constraint that the sum of the mole (or mass) fractions is equal to 1.

Thus, you can conclude that the number of variables N_v needed to specify the condition of a stream completely is given by

$$N_v = N_{sp} + 2 \quad (30.2)$$

You should keep in mind that in a binary system, for example, in which one stream component is zero, for consistency you would count $N_{sp} = 2$ with the one component having a zero value treated as a constraint.

What kinds of equations are involved in the analysis of the degrees of freedom? A list would include

- (1) independent material balances for each species (a total balance could be substituted for one species balance)
- (2) energy balance
- (3) phase equilibria relations, that is, equations that give the compositions between one species that exists in two (or more) phases; refer to Chapter 19
- (4) chemical equilibrium relations.

- (5) implicit relations, such that the concentration of a species is zero in a stream
- (6) explicit relations, such that a given fraction of a stream condenses
- (7) extent of reaction or fraction conversion specified

To illustrate an analysis for the degrees of freedom, examine Figures 30.2A and B, which show a simple steady-state isothermal, isobaric process involving three streams plus heat transfer. The count of the variables and equations is

Variables:

$(N_{sp} + 2) \times 3 = (2 + 2) \times 3 =$	12
Q	1
Total	<u>13</u>

Equations:

Material balances	2
Energy balance	1

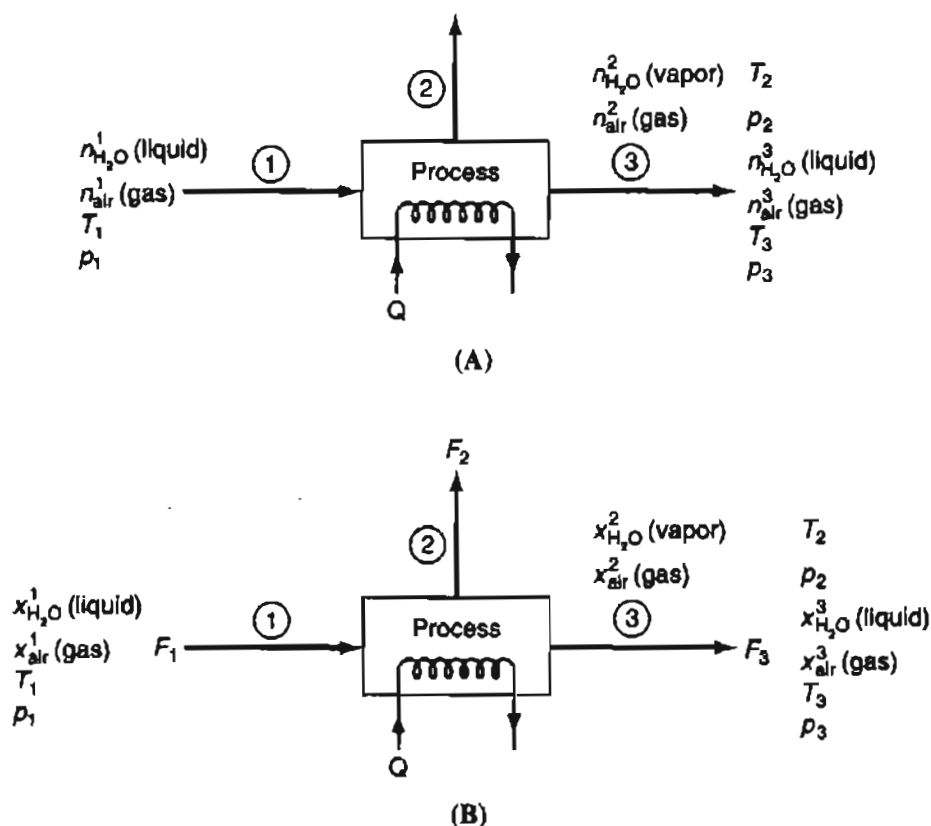


Figure 30.2 A simple process with three streams. In Figure 30.2A the stream flows are expressed as mole flow rates, and in Figure 30.2B the stream flow is the total flow and the compositions of the species are given in mole fractions.

Phase equilibrium for H_2O	1
T is the same in all 3 streams	
$(T_1 = T_2 = T_3)$ 2 independent equations	2
p is the same in all 3 streams	
$(T_1 = T_2 = T_3)$ 2 independent equations	2
Total	8

Degrees of freedom:

$$13 - 8 = 5$$

The way in which the compositions are specified makes no difference in the analysis.

We now take up five simple processes in Example 30.1, and evaluate the number of degrees of freedom for each.

EXAMPLE 30.1 Determining the Degrees of Freedom in a Process

We shall consider five typical processes, as depicted by the respective figures below, and for each ask the question: How many variables have to be specified [i.e., what are the degrees of freedom (N_d)] to make the problem of solving the combined material and energy balances determinate? All the processes will be steady-state, and the entering and exit streams single-phase streams.

(a) **Stream splitter** (Figure E30.1a): We assume that $Q = W = 0$, and that the energy balance is not involved in the process. By implication of a splitter, the temperatures, pressures, and the compositions of the inlet and outlet streams are identical. The count of the total number of variables, total number of constraints, and degrees of freedom is as follows:

Total number of variables		
$N_v = 3(N_{sp} + 2) =$	$3(N_{sp} + 2)$	
Number of independent equations		
Material balances	1	
Compositions of Z , P_1 , and P_2		
are the same	$2(N_{sp} - 1)$	
$T_{P1} = T_{P2} = T_Z$	2	
$p_{P1} = p_{P2} = p_Z$	2	
Total number of degrees of freedom		$\frac{2N_{sp} + 3}{N_{sp} + 3}$

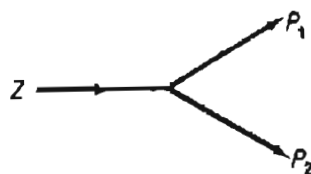


Figure E30.1a

Did you note that we only counted N_{sp} material balances once? Why? Let us look at some of the balances:

$$\text{Component 1: } Zx_{1Z} = P_1x_{1P_1} + P_2x_{1P_2}$$

$$\text{Component 2: } Zx_{2Z} = P_1x_{2P_1} + P_2x_{2P_2}$$

etc.

If $x_{1Z} = x_{1P_1} = x_{1P_2}$ and the same is true for x_2 , and so on, only one independent material balance exists.

Do you understand the counts resulting from making the compositions equal in Z , P_1 , and P_2 ? Write down the expressions for each component: $x_{iZ} = x_{iP_1} = x_{iP_2}$. Each set represents $2N_{sp}$ constraints. But you cannot specify every x_i in a stream, only $N_{sp} - 1$ of them. Do you remember why?

To make the problem determinate we might specify the values of the following decision variables:

Flow rate Z	1
Composition of Z	$N_{sp} - 1$
T_Z	1
P_Z	1
Ratio of split $\alpha = P_1/P_2$	1
Total number of degrees of freedom	<u><u>$N_{sp} + 3$</u></u>

(b) **Mixer** (Figure E30.1b): For this process we assume that $W = 0$, but Q is not.

$$\text{Total number of variables (3 streams + } Q) \quad 3(N_{sp} + 2) + 1$$

Number of independent equations

Material balances

N_{sp}

Energy balance

1

$$\begin{aligned} \text{Total number of degrees of freedom} &= 3(N_{sp} + 2) + 1 - (N_{sp} + 1) \\ &= 2N_{sp} + 6 \end{aligned}$$

(c) **Heat exchanger** (Figure E30.1c): For this process we assume that $W = 0$ (but not Q).

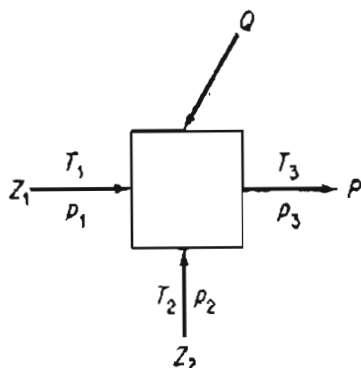


Figure E30.1b

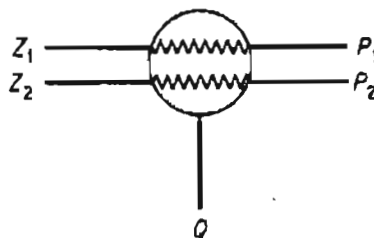


Figure E30.1c

Total number of variables

$$N_v = 4(N_{sp} + 2) + 1 =$$

$$4N_{sp} + 9$$

Number of independent equations

Material balances (streams 1 and 2)

$$2$$

Energy balance

$$1$$

Composition of inlet and outlet

streams the same

$$\frac{2(N_{sp} - 1)}{}$$

$$\frac{2N_{sp} + 1}{}$$

Total number of degrees of freedom =

$$\frac{2N_{sp} + 8}{}$$

One might specify four temperatures, four pressures, $2(N_{sp} - 1)$ compositions in Z_1 and Z_2 , and Z_1 and Z_2 themselves to use up $2N_{sp} + 8$ degrees of freedom.

(d) **Pump** (Figure E30.1d): Here $Q = 0$ but W is not.

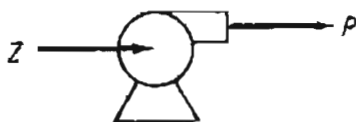


Figure E30.1d

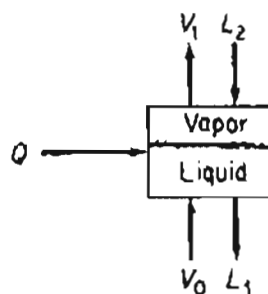


Figure E30.1e

Total number of variables

$$N_v = 2(N_{sp} + 2) + 1$$

$$2N_{sp} + 5$$

Number of independent equations

Material balances

$$1$$

Composition of inlet and outlet

streams the same

$$\frac{N_{sp} - 1}{}$$

Energy balance

$$1$$

$$\frac{N_{sp} + 1}{}$$

Total number of degrees of freedom

$$\frac{N_{sp} + 4}{}$$

(e) **Two-phase well-mixed tank (stage) at equilibrium** (Figure E30.1e) (L , liquid phase; V , vapor phase): Here $W = 0$. Although two phases exist (V_1 and L_1) at equilibrium inside the system, the streams entering and leaving are single-phase streams. By equilibrium we mean that both phases are at the same temperature and pressure and that an equation is known that relates the composition in one phase to that in the other for each component.

Total number of variables (4 streams + Q)

$$4(N_{sp} + 2) + 1$$

Number of independent equations

Material balances

$$N_{sp}$$

Energy balance	1
Composition relations at equilibrium	N_{sp}
Temperatures of the streams V_1 and L_1 in the two phases equal	1
Pressures of the streams V_1 and L_1 in the two phases equal	1
	<hr/>

$$\text{Total number of degrees of freedom} = 4(N_{sp} + 2) + 1 - 2N_{sp} - 3 = 2N_{sp} + 6$$

In general you might specify the following variables to make the problem determinate:

Input stream L_2	$N_{sp} + 2$
Input stream V_0	$N_{sp} + 2$
Pressure	1
Q	1
Total	$2N_{sp} + 6$

Other choices are of course possible, but such choices must leave the equality constraints independent.

EXAMPLE 30.2 Proper Process Specification

Figure E30.2 shows an isothermal separations column. At present the column specifications call for the feed mass fractions to be $\omega_{C_4} = 0.15$, $\omega_{C_5} = 0.20$, $\omega_{iC_5} = 0.30$, and $\omega_{C_6} = 0.35$; the overhead mass fractions to be $\omega_{C_5} = 0.40$ and $\omega_{C_6} = 0$; and the residual product mass fraction to be $\omega_{C_4} = 0$. Unless specified as 0, the component exists in a stream.

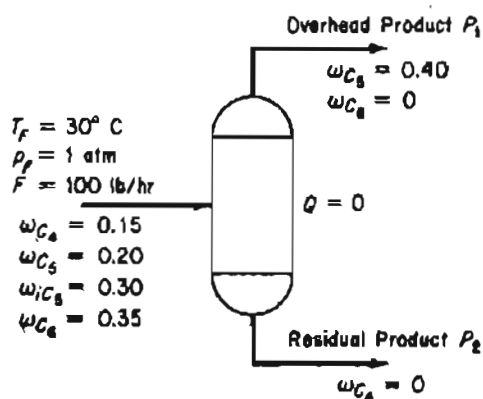


Figure E30.2

Given that $F = 100$ lb/hr, is the separator completely specified, that is, are the degrees of freedom $N_d = 0$? The streams P_1 and P_2 are not in equilibrium.

Solution

First we calculate N_v and then N_e . We will assume that all the stream temperatures and pressures are identical. Number of variables N_v :

$$N_v = (N_{sp} + 2)(3) = (4 + 2)(3) = \underline{18}$$

Number of restrictions and equations give N_e :

$$\text{Component mass balances (no reaction)} = N_{sp} = 4$$

$$T_F = T_{P1} = T_{P2} \quad 2$$

$$p_F = p_{P1} = p_{P2} \quad 2$$

Initial column specifications:

$$(4 \text{ in. } F, 2 \text{ in. } P_1, \text{ and } 1 \text{ in. } P_2 \text{ plus } T_F = 30^\circ\text{C and } p_F = 1 \text{ atm}) \quad 9$$

$$\text{Total for } N_e \quad \underline{17}$$

$$\text{Number of degrees of freedom } N_d: 18 - 17 = 1$$

Note that only four factors can be specified in stream F , namely the rate of F itself and three ω 's; one of the ω 's is redundant. One more variable must be specified for the process, but one that will not reduce the number of independent equations and restrictions already enumerated.

So far we have examined single units without a reaction occurring in the unit. How is the count for N_d affected by the presence of a reaction in the unit? The way N_v is calculated does not change except to add one extent of reaction variable for each reaction in the minimal set (refer to Chapter 10) if species balances are going to be used. As to N_e , all restrictions are deducted from N_v that represent *independent* restrictions on the unit. Thus the number of equations is not necessarily equal to the number of species (H_2O , O_2 , CO_2 , etc.) but instead is the number of independent equations that exist determined in the same way as we did in Chapters 8 to 13. Fixed ratios of materials such as the O_2/N_2 ratio in air or the CO/CO_2 ratio in a product gas would be a restriction, as would be a specified conversion fraction or a known molar flow rate of a material. If some degrees of freedom exist still to be specified, improper specification of a variable may disrupt the independence of equations and/or specifications previously enumerated in the enumeration of N_e , so be careful.

EXAMPLE 30.3 Degrees of Freedom for a Process with a Reaction Taking Place in the System Using Element Balances

A classic reaction for producing H_2 is the so-called "water gas shift" reaction:

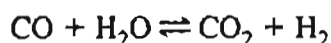


Figure E30.3 shows the process data and the given information. How many degrees of freedom remain to be satisfied? For simplicity assume that the temperature and

pressures of all entering and exit streams are the same and that all streams are gases. The amount of water in excess of that needed to convert all the CO completely to CO_2 is prespecified. Work = 0.

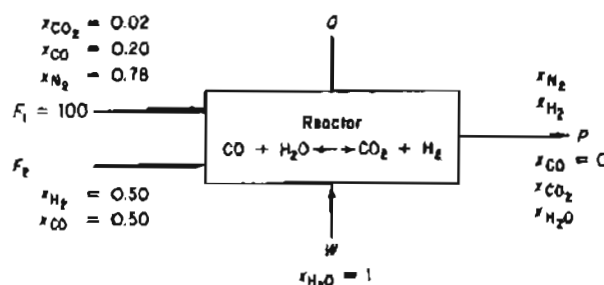


Figure E30.3

Solution

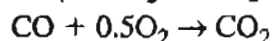
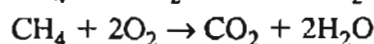
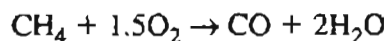
Let us use element material balances rather than species balances in the analysis.

$N_v = 4(N_{sp} + 2) + 1 = 4(5 + 2) + 1 =$	<u>29</u>
(+ 1 is for Q)	
N_e Independent material balances	
(C, O, N, H)	4
Energy balance	1
$T_{F_1} = T_{F_2} = T_W = T_P$	3
$p_{F_1} = p_{F_2} = p_W = p_P$	3
Compositions and flows specified:	
In F_1 ($x_{\text{H}_2\text{O}} = x_{\text{H}_2} = 0$) including F_1	5
In F_2 ($x_{\text{N}_2} = x_{\text{CO}_2} = x_{\text{H}_2\text{O}} = 0$)	4
In W (all but $x_{\text{H}_2\text{O}}$ are 0) only 4 of 5 x_i 's are independent	4
In P ($x_{\text{CO}} = 0$)	1
Specified W	<u>1</u>
$N_d = 29 - 26 =$	<u>26</u> 3

In the streams F_2 and W , only four compositions can be specified; a fifth specification is redundant. The total flows are not known. The given value of the excess water provides the information about the reaction products. Certainly, the temperature and pressure need to be specified, absorbing two degrees of freedom. The remaining degree of freedom might be the N_2/H_2 ratio in P , or the value of F_2 , or the ratio of F_1/F_2 , and so on.

EXAMPLE 30.4 Degrees of Freedom for a Process Involving Multiple Reactions Using Species Balances

Methane burns in a furnace with 10% excess air, but not completely, so some CO exits the furnace, but no CH_4 exits. The reactions are:



Carry out a degree-of-freedom analysis for this combustion problem.

Solution

For this example we will use species material balances in the analysis.

Figure 30.4 shows the process; all streams are assumed to be gases. Only two of the reactions are independent. Q is a variable here. For simplicity assume that the entering and exit streams are at the same temperatures and pressures.

$$N_v = 3(6 + 2) + 1 + 2 = \underline{27}$$

(+1 is for Q and +2 for the extent of reactions)

N_e	Species material balances	6	
	Energy balance	1	
	$T_A = T_F = T_P$	2	
	$P_A = P_F = P_P$	2	
	Compositions specified:		
	In A ($N_{sp} - 1$) some 0	5	
	In F ($N_{sp} - 1$) some 0	5	
	In P	1	11
	Percent excess air i.e., A :		$\frac{1}{11}$
			<u>23</u>

$$N_d = 27 - 23 = 4$$

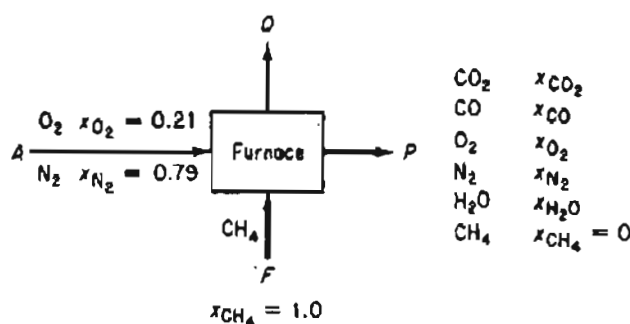


Figure E30.4

To have a well-defined problem you should specify (a) the temperature, (b) the pressure, (c) either the feed rate, or the air rate, or the product rate, and (d) either the CO/CO_2 ratio or the fraction of CH_4 converted to CO or alternatively to CO_2 .

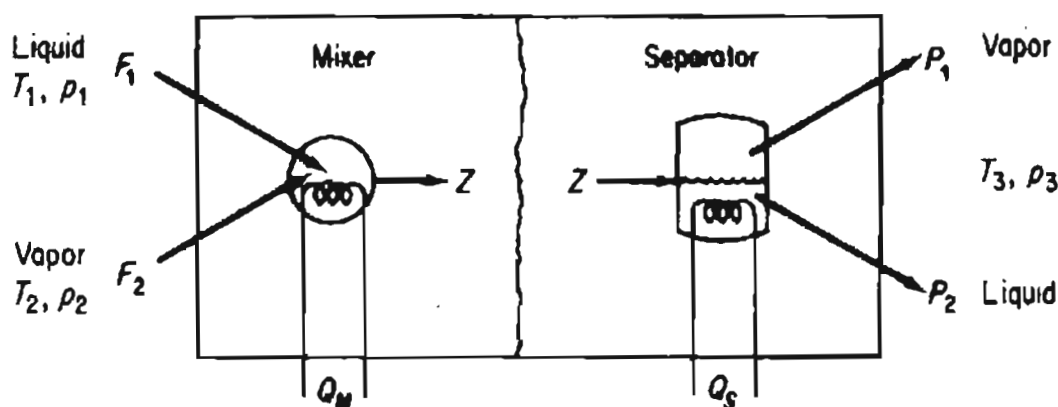


Figure 30.3 Degrees of freedom in combined units.

You can compute the degrees of freedom for combinations of like or different simple processes by proper combination of their individual degrees of freedom. In adding the degrees of freedom for units, you must eliminate any double counting either for variables or constraints, and take proper account of interconnecting streams whose characteristics are often fixed only by implication.

Examine the mixer-separator in Figure 30.3. For the mixer considered as a separate unit, from Example 30.1b, $N_d = 2N_{sp} + 6$. For the separator, an equilibrium unit:

$N_v = 3(N_{sp} + 2) + 1 =$	$3N_{sp} + 7$
N_c :	
Material balances	N_{sp}
Equilibrium relations	N_{sp}
Energy balance	1
$T_Z = T_{P_1} = T_{P_2}$	2
$p_Z = p_{P_1} = p_{P_2}$	2
	$2N_{sp} + 5$
$N_d = (3N_{sp} + 7) - (2N_{sp} + 5) =$	$N_{sp} + 2$

The sum of the mixer and separator is $3N_{sp} + 8$.

You must deduct redundant variables and add redundant restrictions as follows:

Redundant variables:	
Remove 1 Q	1
Remove Z	$N_{sp} + 2$
Redundant constraints:	
1 energy balance	1

Then $N_d = (3N_{sp} + 8) - (N_{sp} + 3) + 1 = 2N_{sp} + 6$, the same as in Example 30.1e.

EXAMPLE 30.5 Degrees of Freedom in a System Composed of Several Units

Ammonia is produced by reacting N_2 and H_2 :

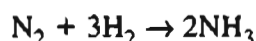


Figure E30.5a shows a simplified flowsheet. All the units except the separator and lines are adiabatic. The liquid ammonia product is essentially free of N_2 , H_2 , and A. Assume that the purge gas is free of NH_3 . Treat the process as four separate units for a degree-of-freedom analysis, and then remove redundant variables and add redundant constraints to obtain the degrees of freedom for the overall process. The fraction conversion in the reactor is 25%.

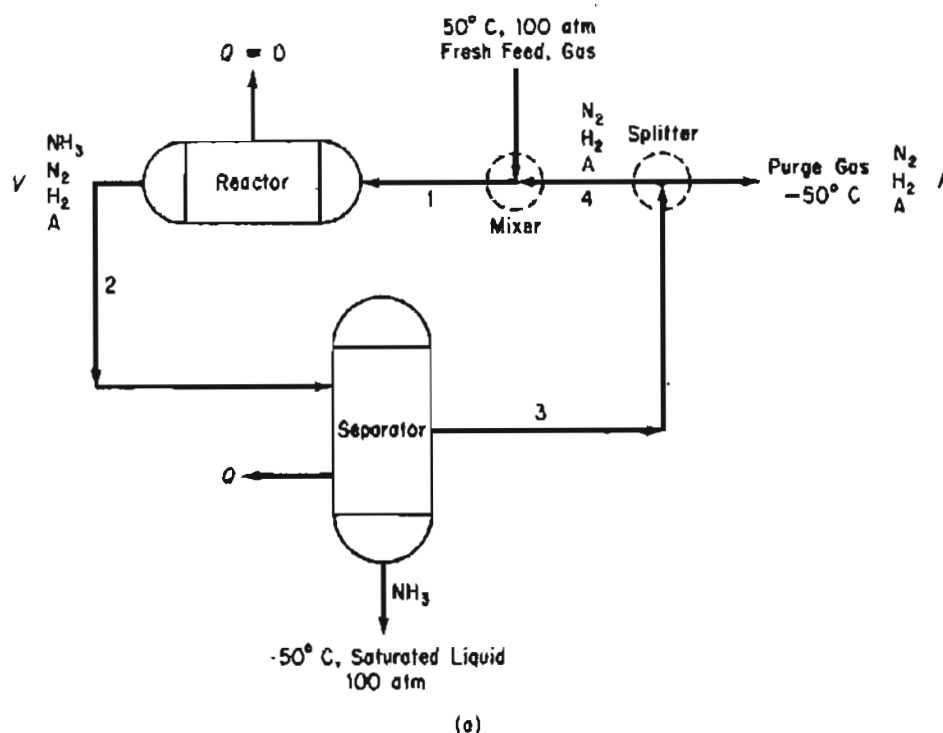


Figure E30.5a

Solution

Mixer:

$$N_v = 3(N_{sp} + 2) + 1 = 3(6) + 1 = 19$$

N_e :

Material balances (H_2 , N_2 , A only) 3

Energy balance 1

Specifications:

NH_3 concentration is zero 3

$T_P = -50^\circ C$ 1

$T_F = 50^\circ C$ 1

Assume that $p_F = p_{\text{mix out}} = p_{\text{split}} = 100$	3	
$Q = 0$	1	<u>13</u>
$N_d = 19 - 13 =$		<u><u>6</u></u>

Reactor:

$N_v = 2(N_{sp} + 2) + 1 = 2(6) + 1 + 1$ (for ξ) =	14
N_e :	
Material balances (H, N, NH_3 , A)	4
Energy balances	1
Specifications:	
NH_3 entering = 0	1
$Q = 0$	1
Fraction conversion	1
$p_{\text{in}} = p_{\text{out}} = 100$ atm	2
Energy balance	1
$N_d = 14 - 11 =$	<u><u>3</u></u>

Separator:

$N_v = 3(N_{sp} + 2) + 1 = 3(6) + 1 =$	19
N_e :	
Material balances	4
Energy balance	1
Specifications:	
$T_{\text{out}} = -50^\circ \text{C}$	1
$p_r = p_{\text{in}} = p_{\text{NH}_3} = 100$	3
NH_3 concentration is 0 in recycle gas	1
$\text{N}_2, \text{H}_2, \text{A}$ are 0 in liquid NH_3	3
$N_d = 19 - 13 =$	<u><u>6</u></u>

Splitter:

$N_v = 3(N_{sp} + 2) = 3(6) =$	18
N_e :	
Material balances	1
Specifications:	
NH_3 concentration = 0	1
Compositions same $2(N_{sp} - 1)$	6
Stream temperatures same = -50°C	3
Stream pressures same = 100 atm	3
$N_d = 18 - 14 =$	<u><u>4</u></u>

The total number of degrees of freedom is 19 less the redundant information, which is as follows:

Redundant variables in interconnecting streams being eliminated:

$$\text{Stream 1: } (4 + 2) = 6$$

$$\text{Stream 2: } (4 + 2) = 6$$

$$\text{Stream 3: } (4 + 2) = 6$$

$$\text{Stream 4: } (4 + 2) = 6$$

$$\underline{24}$$

Redundant constraints being eliminated:

Stream 1:

$$\text{NH}_3 \text{ concentration} = 0 \quad 1$$

$$p = 100 \text{ atm} \quad 1$$

Stream 2:

$$p = 100 \text{ atm} \quad 1$$

Stream 3:

$$\text{NH}_3 \text{ concentration} = 0 \quad 1$$

$$p = 100 \text{ atm} \quad 1$$

$$T = -50^\circ \text{C} \quad 1$$

Stream 4:

$$\text{NH}_3 \text{ concentration} = 0 \quad 1$$

$$T = -50^\circ \text{C} \quad 1$$

$$p = 100 \text{ atm} \quad \underline{1}$$

$$\underline{9}$$

Overall the number of degrees of freedom should be

$$N_d = 19 - 24 + 9 = 4$$

We can check the count for N_d by making a degrees-of-freedom analysis about the entire process as follows:

Examine Figure E30.5b.

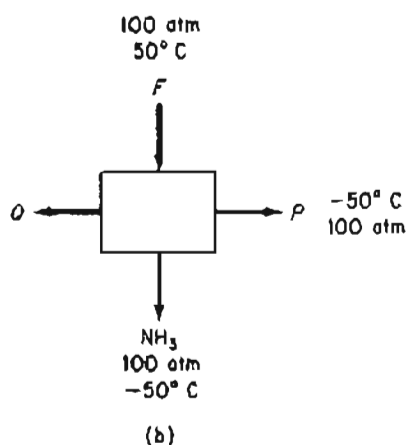


Figure E30.5b

$$N_v = 3(4 + 2) + 1 + 1 \text{ (for } \xi) = 20$$

N_e :

Material balances

(H_2 , N_2 , NH_3 , A)

4

Energy balance	1	
Specifications:		
Stream F ($T = 50^\circ\text{C}$, $p =$ 100 atm, $\text{NH}_3 = 0$)	3	
NH_3 stream ($T = -50^\circ\text{C}$, $p = 100$ atm, three components have 0 concentration)	5	
Purge stream ($T = -50^\circ\text{C}$, $p = 100$ atm, $\text{NH}_3 = 0$)	3	16
$N_d = 20 - 16 =$		<u>4</u>

We do not have the space to illustrate additional combinations of simple units to form more complex units, but Kwauk¹ prepared several excellent tables summarizing the variables and degrees of freedom for distillation columns, absorbers, heat exchangers, and the like. Also read the references at the end of this chapter.

Looking Back

In this chapter we described how to determine the number of degrees of freedom involved in a process, i.e., the number of additional values of variables that have to be specified to get a solution to a problem.

SELF-ASSESSMENT TEST

1. Is there any difference between the number of species present in a process and the number of components in the process?
2. Why are there $N_{sp} + 2$ variables associated with each stream?
3. Determine the number of degrees of freedom for a still (see Figure SAT30.1P3).

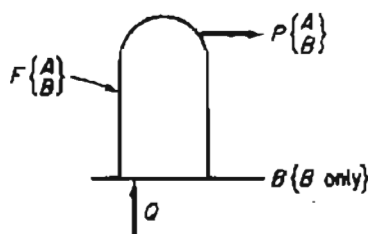


Figure SAT30.1P3

¹M. Kwauk. *AIChE J.*, 2, (1956): 2.

4. Determine the number of degrees of freedom in the following process (Figure SAT30.1P4):

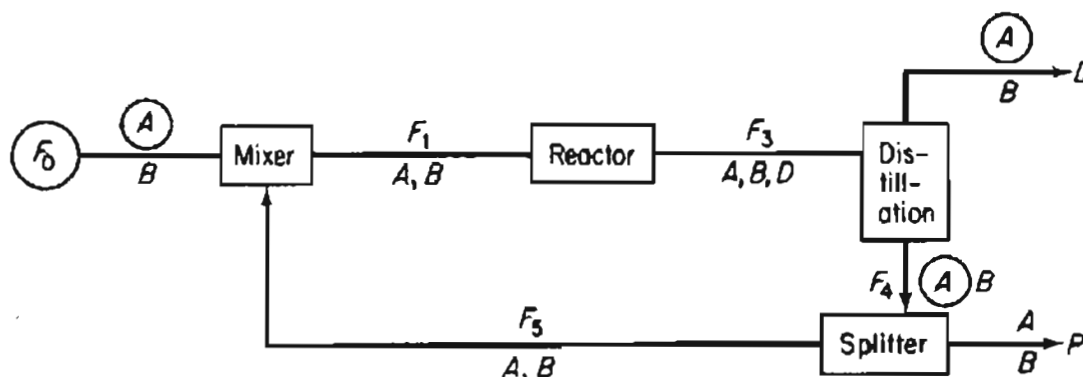


Figure SAT30.1P4

The encircled variables have known values. The reaction parameters in the reactor are known as is the fraction split at the splitter between F_4 and F_5 . Each stream is a single phase.

5. Figure SAT30.1P5 represents the schematic flowsheet of a distillation tower used to recover gasoline from the products of a catalytic cracker. Is the problem completely specified, that is, is the number of degrees of freedom equal to zero for the purpose of calculating the heat transfer to the cooling water in the condenser?

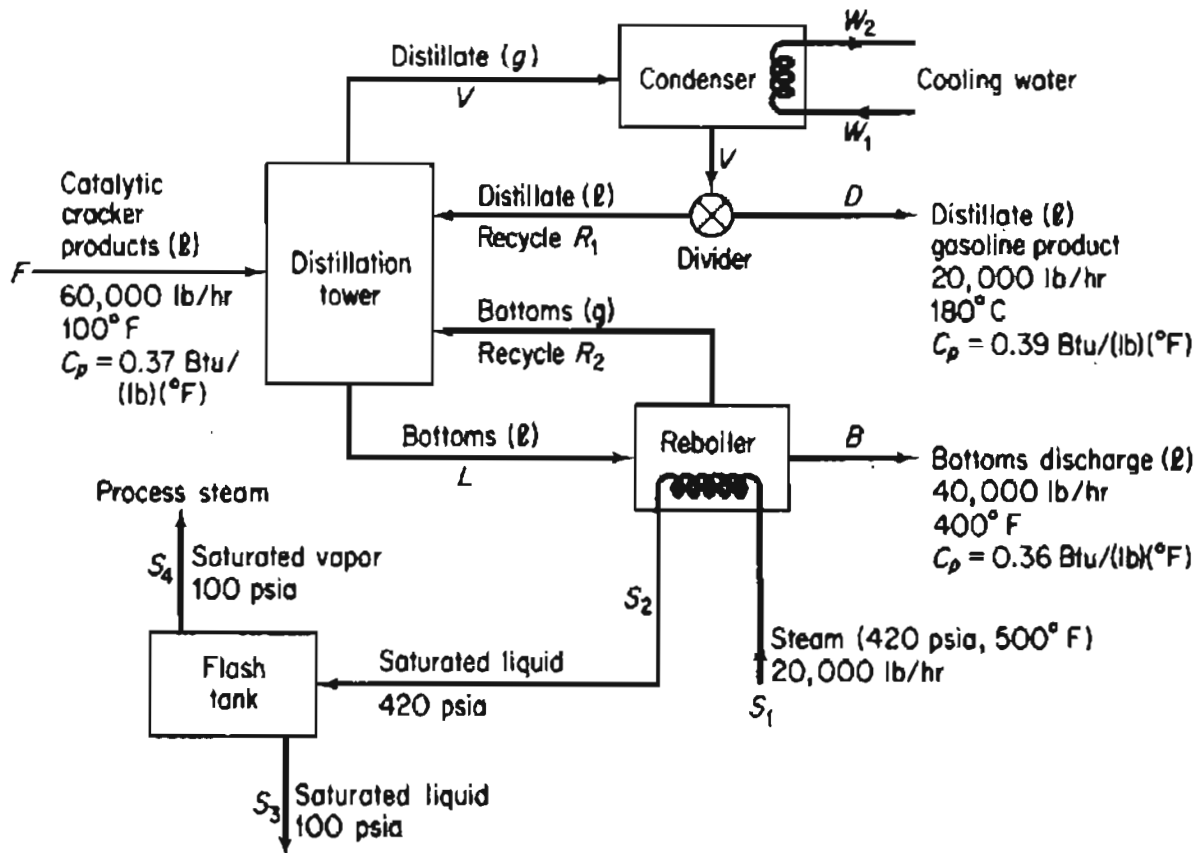


Figure SAT30.1P5

Thought Problems

1. If one or more of the variables in a process can take on only integer values (such as number of stages in a column or number of reactors in a series of reactors), will the analysis of degrees of freedom have to be changed?
2. What other variables in some processes might have to be included in the count of variables for a stream to add to $(N_{sp} + 2)$.

Discussion Question

1. How should a computer code handle the calculation of the degrees of freedom so that a naive user does not overspecify or underspecify the problem?

SUPPLEMENTARY REFERENCES

- Pham, Q. T. "Degrees of Freedom of Equipment and Processes." *Chem. Eng. Sci.*, **49**:2507 (1994).
- Ponton, J. W. "Degrees of Freedom Analysis in Process Control." *Chem. Eng. Sci.*, **49**:2089 (1994).
- Smith, B. D. *Design of Equilibrium Stage Processes*, Chapter 3. New York: McGraw-Hill (1963).
- Sommerfeld, J. T. "Degrees of Freedom and Precedence Orders in Engineering Calculations." *Chem. Eng. Educ.*:138 (Summer, 1986).

PROBLEMS

- 30.1** Determine the number of degrees of freedom for the condenser shown in Figure P30.1.

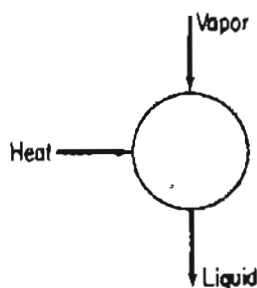


Figure P30.1

- 30.2** Determine the number of degrees of freedom for the reboiler shown in Figure P30.2. What variables should be specified to make the solution of the material and energy balances determinate?

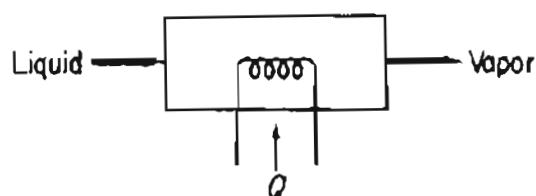


Figure P30.2

- 30.3 If to the equilibrium stage shown in Example 6.1 you add a feed stream, determine the number of degrees of freedom. See Figure P30.3.

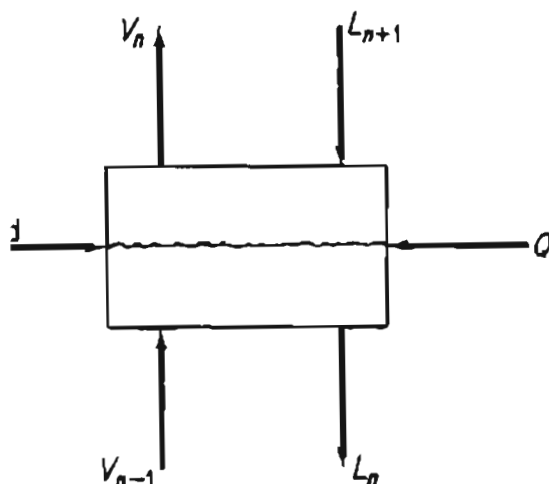


Figure P30.3

- 30.4 How many variables must be specified for the furnace shown in Figure P30.4 to absorb all the degrees of freedom?

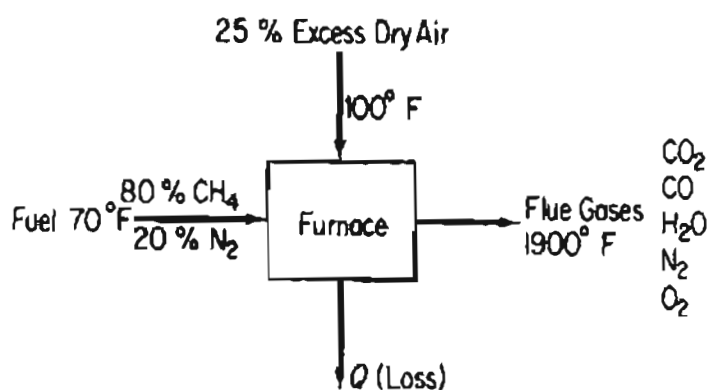


Figure P30.4

- 30.5 Figure P30.5 shows a simple absorber or extraction unit. S is the absorber oil (or fresh solvent), and F is the feed from which material is to be recovered. Each stage has a Q (not shown); the total number of equilibrium stages is N . What is the number of degrees of freedom for the column? What variables should be specified?



Figure P30.5

- 30.6** In a reactor model, rather than assume that the components exit from the reactor at equilibrium, an engineer will specify the r independent reactions that occur in the reactor, and the extent of each reaction, ξ_i . The reactor model must also provide for heating or cooling. How many degrees of freedom are associated with such a reactor model? See Figure P30.6.

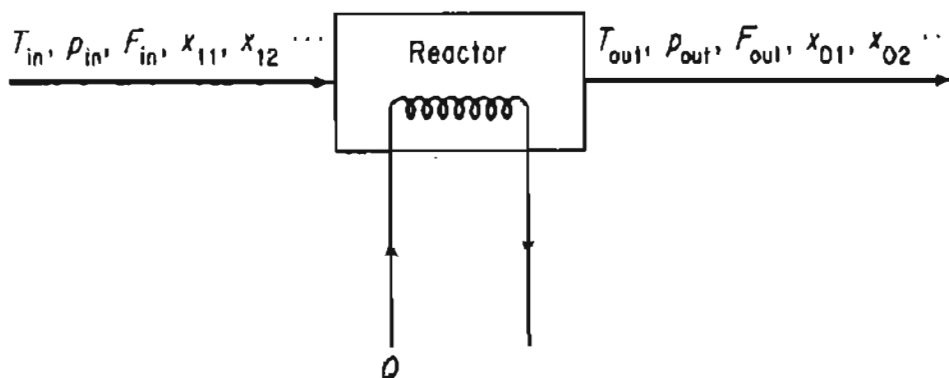


Figure P30.6

- 30.7** Set up decomposition schemes for the processes shown in Figure P30.7. What additional variables must be specified to make the system determinate if (a) the feed conditions are known; or (b) the product conditions are specified?

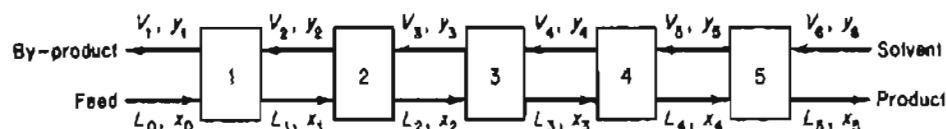


Figure P30.7

- 30.8** Determine whether or not the following problems are determinate in the sense that all the values of the material flows can be calculated.
- A vapor mixture containing 45 weight percent ammonia, the balance being water, and having an enthalpy of 1125 Btu per pound, is to be fractionated in a bubble-cap column operating at a pressure of 250 psia. The column is to be equipped with a total condenser. The distillate product is to contain 99.0 weight percent ammonia and the bottom product is to contain 10.0 weight percent ammonia. The distillate and the reflux leaving the condenser will have an enthalpy of 18 Btu/lb (Figure P30.8a).
 - An engineer designed an extraction unit (Figure P30.8b) to recover oil from a pulp using alcohol as a solvent. The inerts refer to oil-free and solvent-free pulp. Several of the streams are shown as F_0 and F_1 . Notice that the extracts from the first two stages were not clear but contained some inerts. (Both V_1 and V_2 contain all three components: oil, solvent, and inerts.) Equal amounts of S_1 and L_1 were added to stage 2. There are 2 lb of L_2 for each lb of V_2 leaving the second stage.

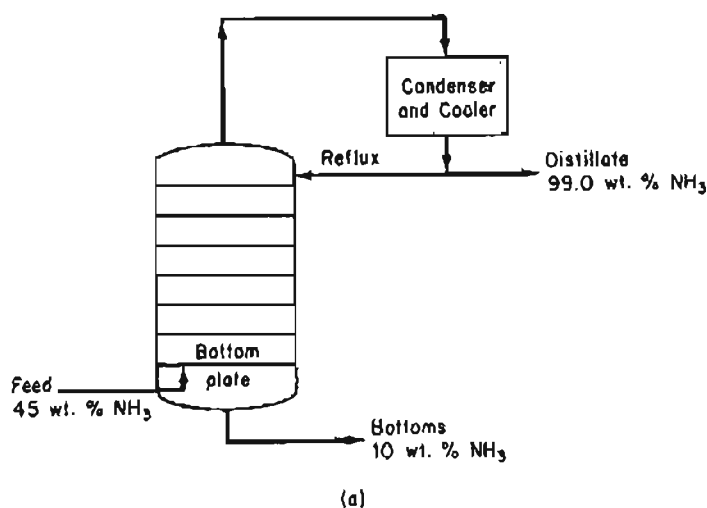


Figure P30.8a

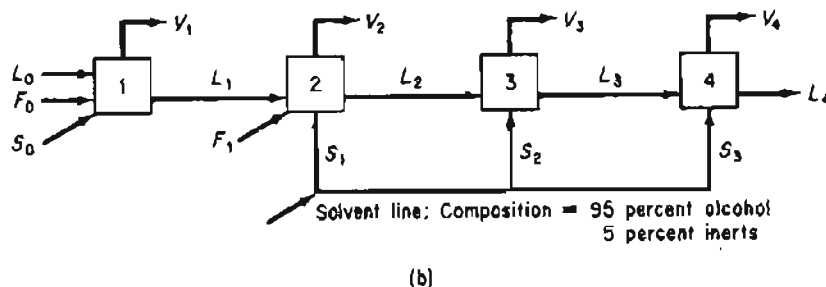
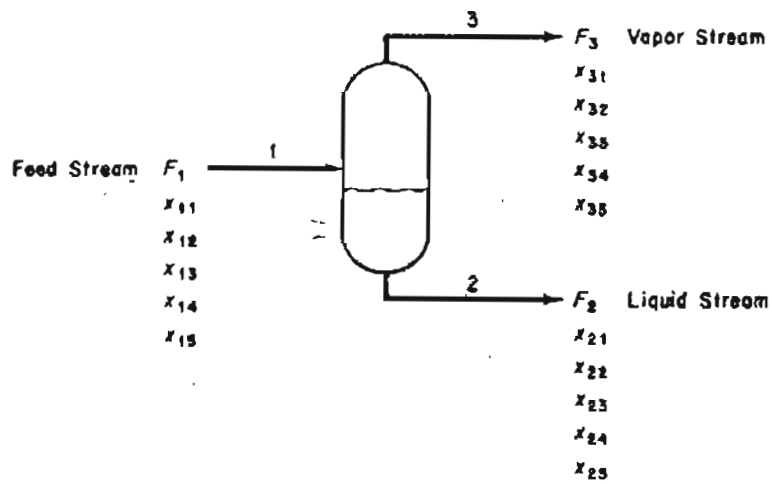


Figure P30.8b

The raffinate from stage 1, L_1 , contains 32.5 percent alcohol and also in this same stream the weight ratio of inerts to solution is 60 lb inert/100 lb solution. The remaining raffinate streams, L_2 , L_3 , and L_4 , contain 60 lb inert/100 lb alcohol. The L_2 stream contains 15 percent oil.

- 30.9** Examine Figure P30.9. Values of F_1 , x_{11} , x_{12} , x_{13} , x_{14} , and x_{15} are known. Streams F_2 and F_3 are in equilibrium, and the three streams all have the same (known) temperatures and pressures. Is the problem completely specified, underspecified, or overspecified? Assume that the values of K in the equilibrium relations can be calculated from the given temperatures and pressures.
- 30.10** Book² describes a mixer-heat exchanger section of a monoethylamine plant that is illustrated in Figure P30.10 along with the notation. Trimethylamine recycle enters in stream 4, is cooled in the heat exchanger, and is mixed with water from stream 1 in mixer 1. The trimethylamine-water mixture is used as the cold-side fluid in the heat exchanger and is then mixed with the ammonia-methanol stream from the gas absorber in mixer 3. The mixture leaving mixer 3 is the reaction mixture which feeds into the preheater of the existing plant.

²N. L. Book. "Structural Analysis and Solution of Systems of Algebraic Design Equations." Ph.D. dissertation, University of Colorado, 1976.



Description of the variables:

F_i - Molar flow for i^{th} stream.

x_{ij} - Mole fraction of j^{th} component in i^{th} stream

K_j - Phase-equilibrium coefficient for the j^{th} component

The design variables are:

The Feed Stream, $F_1, x_{11}, x_{12}, x_{13}, x_{14}$

The Phase-Equilibrium coefficients, K_1, K_2, K_3, K_4, K_5

Figure P30.9

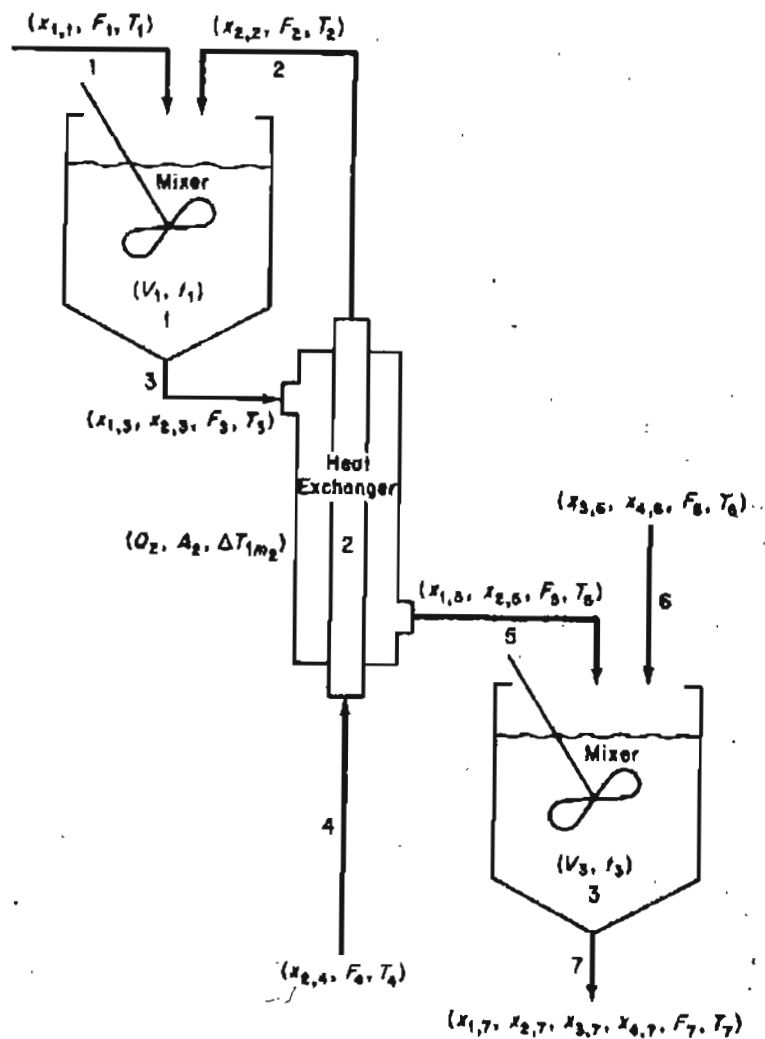


Figure P30.10

Table P30.10 lists the 31 equations that represent the process in Figure P30.10. C_i is a heat capacity (a constant), F_i a flow rate, A area (a constant), ΔT_{lm} a long mean temperature difference

$$\frac{(T_4 - T_5) - (T_2 - T_3)}{\ln[(T_4 - T_5)/(T_2 - T_3)]}$$

U is a heat transfer coefficient (a constant), V_i a volume, y_i the molar flow rate of component i , x_i the mole fraction of component i , Q the heat transfer rate, and ρ_i the molar density (a constant). The question is: How many degrees of freedom exist for the process?

TABLE P30.10 List of Equations to Model the Process

Material Balance Equations

Mole fraction equations

1. $x_{1,1} - 1 = 0$
2. $x_{2,2} - 1 = 0$
3. $x_{1,3} + x_{2,3} - 1 = 0$
4. $x_{2,4} - 1 = 0$
5. $x_{1,5} + x_{2,5} - 1 = 0$
6. $x_{3,6} + x_{4,6} - 1 = 0$
7. $x_{1,7} + x_{2,7} + x_{3,7} + x_{4,7} - 1 = 0$

Flow balance equations

8. $F_1 + F_2 - F_3 = 0$
9. $F_2 - F_4 = 0$
10. $F_3 - F_5 = 0$
11. $F_5 + F_6 - F_7 = 0$

Component balance equations

12. $x_{1,1}F_1 - y_1 = 0$
13. $x_{1,3}F_3 - y_1 = 0$
14. $x_{1,5}F_5 - y_1 = 0$
15. $x_{1,7}F_7 - y_1 = 0$
16. $x_{2,2}F_2 - y_2 = 0$
17. $x_{2,3}F_3 - y_2 = 0$
18. $x_{2,4}F_4 - y_2 = 0$
19. $x_{2,5}F_5 - y_2 = 0$
20. $x_{2,7}F_7 - y_2 = 0$
21. $x_{3,6}F_6 - y_3 = 0$
22. $x_{3,7}F_7 - y_3 = 0$
23. $x_{4,6}F_6 - y_4 = 0$
24. $x_{4,7}F_7 - y_4 = 0$

(continued)

TABLE P30.10 List of Equations to Model the Process (*continued*)

Balance Equations (<i>continued</i>)	
Energy Balance Equations	
25.	$C_1 F_1 T_1 + C_2 F_2 T_2 - C_3 F_3 T_3 = 0$
26.	$C_4 F_4 T_4 - Q_2 - C_2 F_2 T_2 = 0$
27.	$C_3 F_3 T_3 + Q_2 - C_5 F_5 T_5 = 0$
28.	$C_5 F_5 T_5 + C_6 F_6 T_6 - C_7 F_7 T_7 = 0$
Equipment Specification Equations	
29.	$V_1 - (F_3) \left(\frac{V_1}{F_1} \right) / \rho_3 = 0$
30.	$Q_2 - U_2 A_2 (T_{lm2}) = 0$
31.	$V_3 - (F_7) \left(\frac{V_3}{F_3} \right) / \rho_7 = 0$

- 30.11** Cavett proposed the following problems as a test problem for computer-aided design. Four flash drums are connected as shown in Figure P30.11. The temperature in each flash drum is specified, and equilibrium is assumed to be independent of composition so that the vapor-liquid equilibrium constants are truly constant. Is the problem properly specified, or do additional variables have to be given? If the latter, what should they be? The feed is as follows

Component	Feed
1. Nitrogen and helium	358.2
2. Carbon dioxide	4,965.6
3. Hydrogen sulfide	339.4
4. Methane	2,995.5
5. Ethane	2,395.5
6. Propane	2,291.0
7. Isobutane	604.1
8. <i>n</i> -Butane	1,539.9
9. Isopentane	790.4
10. <i>n</i> -Pentane	1,192.9
11. Hexane	1,764.7
12. Heptane	2,606.7
13. Octane	1,844.5
14. Nonane	1,669.0
15. Decane	831.7
16. Undecane plus	1,214.5
Total	27,340.6

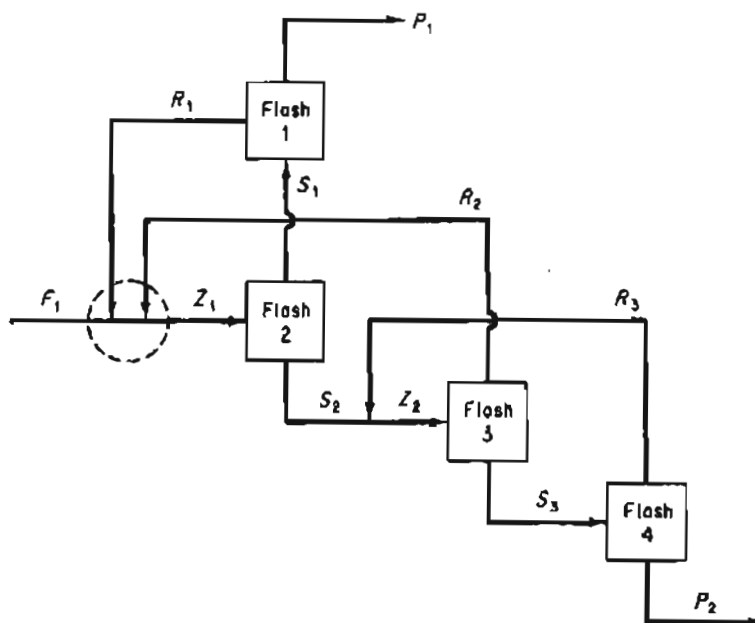


Figure P30.11

- 30.12** The flowsheet (Figure P30.12) has a high-pressure feed stream of gaseous component A contaminated with a small amount of B. It mixes first with a recycle stream consisting mostly of A and passes into a reactor, where an exothermic reaction to form C from A takes place. The stream is cooled to condense out component C and passed through a valve into a flash unit. Here most of the unreacted A and the contaminant B flash off, leaving a fairly pure C to be withdrawn as the liquid stream. Part of the recycle is bled off to keep the concentration of B from building up in the system. The rest is repressurized in a compressor and mixed, as stated earlier, with the feed stream. The number of parameters/variables for each unit are designated by the number within the symbol for the unit. How many degrees of freedom exist for this process?

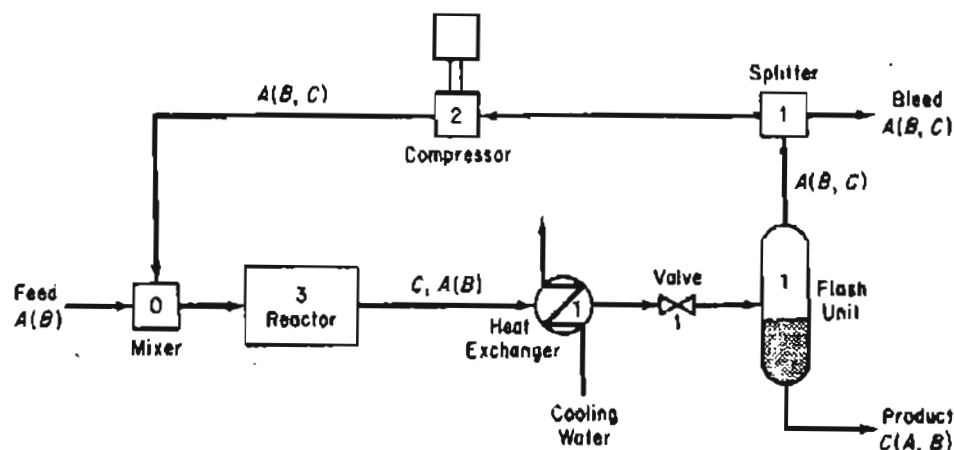


Figure P30.12

CHAPTER 31

SOLVING MATERIAL AND ENERGY BALANCES USING PROCESS SIMULATORS (FLOWSHEETING CODES)

Your objectives in studying this chapter are to be able to:

1. Understand the differences between equation-based and modular-based flowsheeting.
2. How material and energy balances are formulated for equation- and modular-based flowsheeting codes.

Looking Ahead

In this chapter we survey process simulators (flowsheeting codes) that are used in industrial practice to solve material and energy balances.

Main Concepts

As explained in Chapter 11, a plant **flowsheet** such as the simple diagram in Figure 31.1, mirrors the stream network and equipment arrangement in a process. Once the process flowsheet is specified, or during its formulation, the solution of the appropriate process material and energy balances is referred to as **process simulation** or **flowsheeting**, and the computer code used in the solution is known as a **process simulator** or **flowsheeting code**. Codes for both steady state and dynamic processes exist. The essential problem in flowsheeting is to solve (satisfy) a large set of linear and nonlinear equations and constraints to an acceptable degree of precision. Such a program can also, at the same time, determine the size of equipment

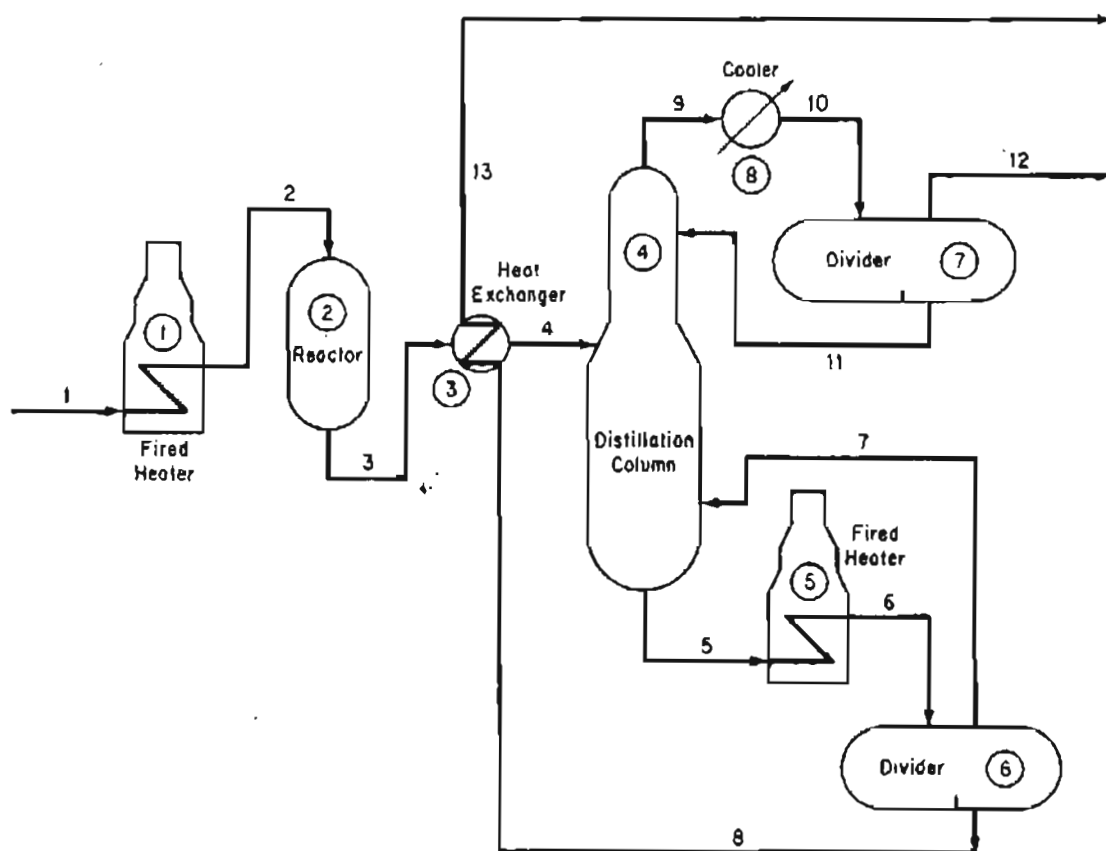


Figure 31.1 Hypothetical process flowsheet showing the materials flow in a process that includes reaction. The encircled numbers denote the unit labels and the other numbers label the interconnecting streams.

and piping, evaluate costs, and optimize performance. Figure 31.2 shows the information flow that occurs in a process simulator.

The software must facilitate the transfer of information between equipment and streams, have access to a reliable database, and be flexible enough to accommodate equipment specifications provided by the user to supplement the library of programs that come with the code. Fundamental to all flowsheeting codes is the calculation of mass and energy balances for the entire process. Valid inputs to the material and energy balance phase of the calculations for the flowsheet must be defined in sufficient detail to determine all the intermediate and product streams and the unit performance variables for all units.

Frequently, process plants contain recycle streams and control loops, and the solution for the stream properties requires iterative calculations. Thus, efficient numerical methods must be used. In addition, appropriate physical properties and thermodynamic data have to be retrieved from a database. Finally, a master program must exist that links all of the building blocks, physical property data, thermodynamic calculations, subroutines, and numerical subroutines, and that also supervises the information flow. You will find that optimization and economic analysis are often the ultimate goal in the use of flowsheeting codes.

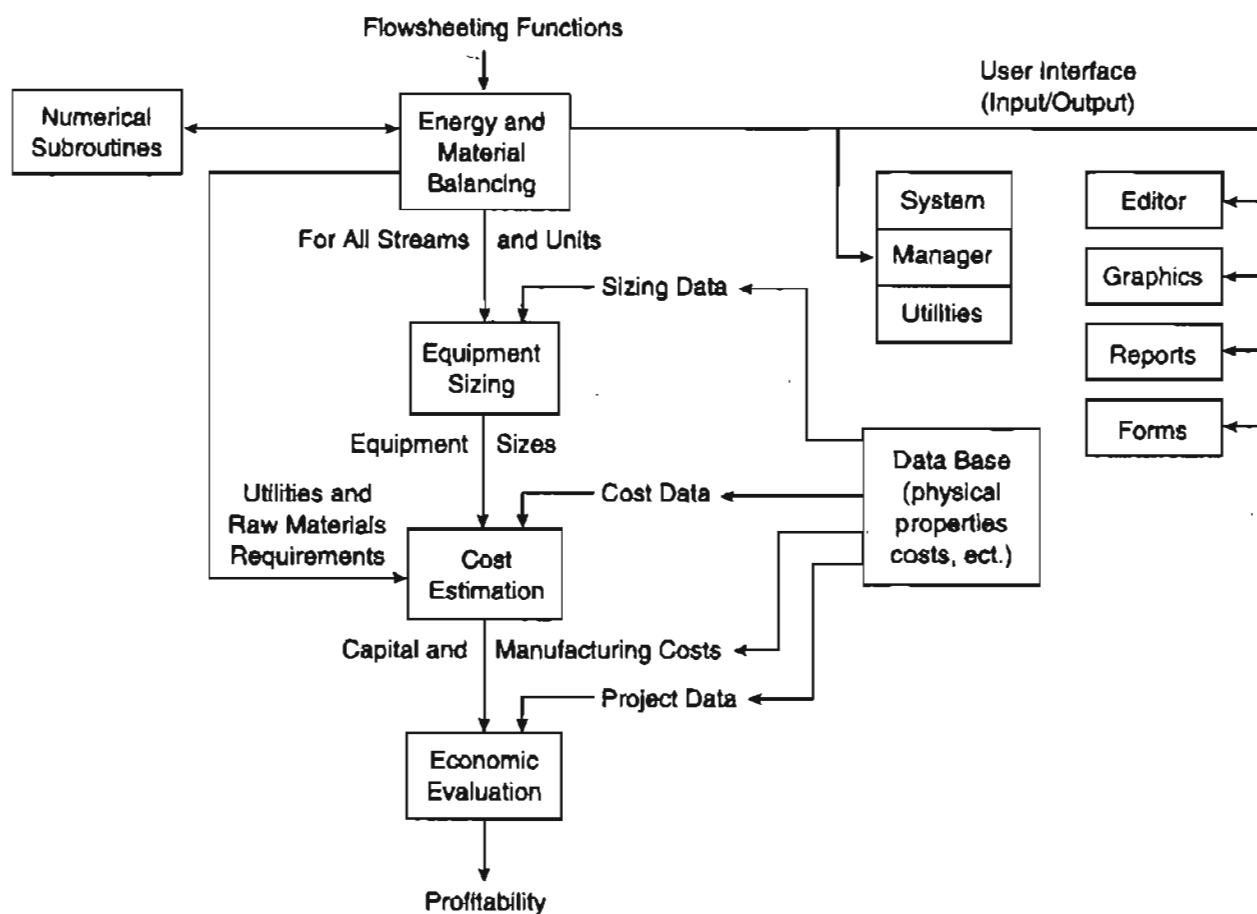


Figure 31.2 Information flow in a typical flowsheeting code.

Other specific applications include

1. Steady and unsteady state simulation to help improve and verify the design of a process and examine complicated or dangerous designs
2. Training of operators
3. Data acquisition and reconciliation
4. Process control, monitoring, diagnostics, and trouble shooting
5. Optimization of process performance
6. Management of information
7. Safety analysis

Typical unit process models found in process simulators for both steady state and unsteady state operations include

1. Reactors of various kinds
2. Phase separation equipment
3. Ion exchange and absorption

4. Drying
5. Evaporation
6. Pumps, compressors, blowers
7. Mixers, splitters
8. Heat exchangers
9. Solid-liquid separators
10. Solid-gas separators
11. Storage tanks

Features that you will find in a general process simulator include

1. Unit and equipment models representing operations and procedures
2. Software to solve material and energy balances
3. An extensive data base of physical properties
4. Equipment sizing and costing functions
5. Scheduling of batch operations
6. Environmental impact assessment
7. Compatibility with auxillary graphics, spreadsheets, and word processing functions
8. Ability to import and export data

Table 31.1 lists some commercial process simulators.

For updated data and information on process simulators refer to <http://www.interduct.tudelft.nl/Pltools/news/news.html>, or to the respective company's web site.

From the viewpoint of a user of a process simulator code you should realize:

TABLE 31.1 Vendors of Commercial Process Simulators

Name of Program	Source
ABACUSII	MIT, Cambridge, Mass.
ASPEN ENGINEERING SUITE (AES)	Aspen Technology, Cambridge, Mass.
CHEMCAD	Chemstations, Houston, Texas
DESIGN II	WinSim, Houston, Texas
D-SPICE	Fantoff Process Technologies
HYSIM, HYSYS	Hyprotech, Calgary, Alberta
PRO/II, PROTISS	Simulation Sciences, Fullerton, California
PROSIM	Bryan Research and Engineering, Bryan, TX
SPEEDUP	Aspen Technology Corp., Cambridge, Mass.
SUPERPRO DESIGNER	Intelligen, Scotch Plains, NJ

1. Several levels of analysis can be carried out beyond just solving material balances including solving material plus energy balances, determining equipment sizing, profitability analysis, and much more. Crude, approximate flowsheets are usually studied before fully detailed flowsheets.
2. The results obtained by simulation rest heavily on the type and validity of the choices you make in selection of the physical property package to be used.
3. You have to realize that the basic function of the process simulator is to solve equations. In spite of the progress made in equation solvers in the last 50 years, the information structure you introduced into the code may yield erroneous or no results. Check essential results by hand. Limits introduced on the range of variable must be valid.
4. A learning curve exists in using a process simulator so that initially a simple problem may take hours to solve whereas as your familiarity with the simulator increases it may only take minutes to solve the same problem.
5. GIGO (Garbage In Garbage Out). You have to take care to put appropriate data and connections between units into the data files for the code. Some diagnostics are provided, but they cannot trouble shoot all of your blunders.

Two extremes exist in process simulator software. At one extreme, the entire set of equations (and inequalities) representing the process is written down, including the material and energy balances, the stream connections, and the relations representing the equipment functions. This representation is known as the **equation-oriented method** of flowsheeting. The equations can be solved in a sequential fashion analogous to the modular representation described below, or simultaneously by Newton's method (or the equivalent), or by employing sparse matrix techniques to reduce the extent of matrix manipulations; you can find specific details in the references at the end of this chapter.

At the other extreme, the process can be represented by a collection of modules (**the modular method of flowsheeting**) in which the equations (and other information) representing each subsystem or piece of equipment are collected together and coded so that the module may be used in isolation from the rest of the flowsheet and hence is portable from one flowsheet to another, or can be used repeatedly in a given flowsheet. A module is a model of an individual element in a flowsheet (such as a reactor) that can be coded, analyzed, debugged, and interpreted by itself. In its usual formulation it is an input-output model, that is given the input values, the module calculates the output values, but the reverse calculation is not feasible. Units represented solely by equations sometimes can yield inputs given the outputs. Some modular based software codes such as Aspen Plus integrate equations with modules to speed up the calculations.

Another classification of flowsheeting codes focuses on how the equations or modules are solved. One treatment is to solve the equations or modules sequentially,

and the other to solve them simultaneously. Either the program and/or the user must select the decision variables for recycle, and provide estimates of certain stream values to make sure that convergence of the calculations occurs, especially in a process with many recycle streams.

A third classification of flowsheeting codes is whether they solve steady-state or dynamic problems. We consider only the former here.

We will review equation-based process simulators first, although historically modular-based codes were developed first, because they are much closer to the techniques described up to this point in this book, and then turn to consideration of modular-based flowsheeting.

a. Equation-Based Process Simulation

Sets of linear and/or nonlinear equations can be solved simultaneously using an appropriate computer code. Equation-based flowsheeting codes have some advantages in that the physical property data needed to obtain values for the coefficients in the equations are transparently transmitted from a database at the proper time in the sequence of calculations. Figure 31.3 shows the information flow corresponding to the flowsheet in Figure 31.1.

Figure 31.4 is a set of equations that represents the basic operation of a flash drum.

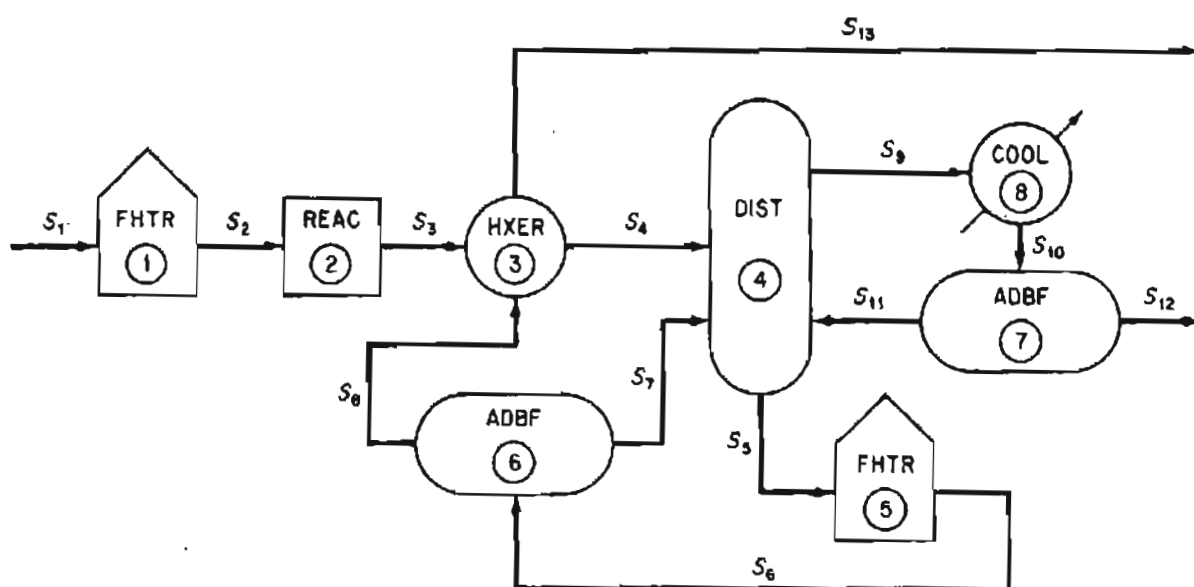
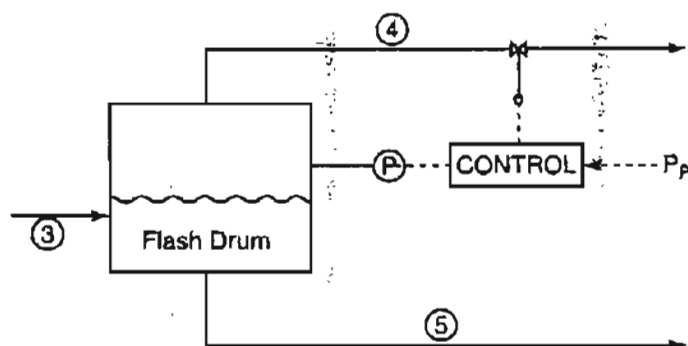


Figure 31.3 Information flow sheet for the hypothetical process in Figure 31.1 (S stands for stream; module or computer code number is encircled).



Material balances:

$$x_{A3}F_3 - y_{A4}F_4 - x_{A5}F_5 = 0$$

$$x_{P3}F_3 - y_{P4}F_4 - x_{P5}F_5 = 0$$

$$x_{G3}F_3 - y_{G4}F_4 - x_{G5}F_5 = 0$$

$$y_{A4} + y_{P4} + y_{G4} = 1$$

$$x_{A5} + x_{P5} + x_{G5} = 1$$

Equilibrium relations:

$$T_4 = T_5$$

$$y_{A4} = K_A x_{A5}$$

$$y_{P4} = K_P x_{P5}$$

$$y_{G4} = K_G x_{G5}$$

$$\text{where } K_i = p_i^*(T_4)/P_F \quad (i = A, P, G)$$

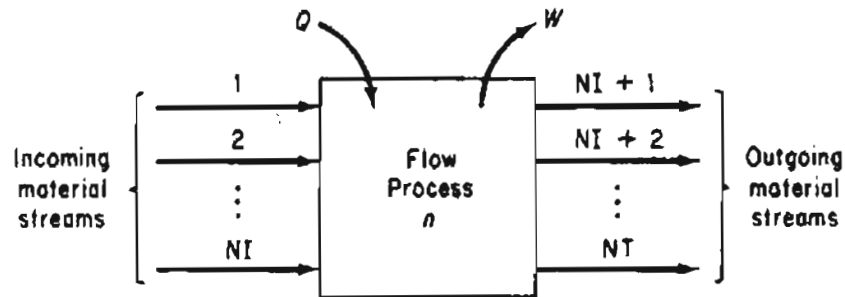
Energy balance:

$$F_5(x_{A5}C_A + x_{P5}C_P + x_{G5}C_G)T_5 = F_5(x_{A5}C_A + x_{P5}C_P + x_{G5}C_G)T_5 + F_4[(y_{A4}C_A + y_{P4}C_P + y_{G4}C_G)T_4 + y_{A4}\lambda_A + y_{P4}\lambda_P + y_{G4}\lambda_G]$$

Figure 31.4 A set of a linear and two nonlinear equations representing a system of three components, A, P, and E, passing through a flash drum.

The interconnections between the unit modules may represent information flow as well as material and energy flow. In the mathematical representation of the plant, the interconnection equations are the material and energy balance flows between model subsystems. Equations for models such as mixing, reaction, heat exchange, and so on, must also be listed so that they can be entered into the computer code used to solve the equation. Figure 31.5 (and Table 31.2) lists the common type of equations that might be used for a single subsystem.

In general, similar process units repeatedly occur in a plant, and can be represented by the same set of equations that differ only in the names of variables, the number of terms in the summations, and the values of any coefficients in the equations.

System diagramTotal mass balance (or mole balance) without reaction)

$$\sum_{i=1}^{NI} F_i = \sum_{i=NI+1}^{NT} F_i$$

Energy Balance

$$\sum_{i=1}^{NI} F_i H_i + Q_n - W_{s,n} = \sum_{i=NI+1}^{NT} F_i H_i$$

Vapor-liquid equilibrium distribution

$$y_j = K_j x_j \quad \text{for } j = 1, 2, \dots, NC$$

Equilibrium vaporization coefficients

$$K_j = K(T_i, P_i, \bar{W}_i) \quad j = 1, 2, \dots, NC$$

Component mass or mole balances

$$\sum_{i=1}^{NI} F_i w_{i,j} = \sum_{i=NI+1}^{NT} F_i w_{i,j} \quad \text{for } j = 1, 2, \dots, NC$$

Summation of mole or mass fractions

$$\sum_{j=1}^{NC} w_{i,j} = 1.0 \quad \text{for } i = 1, 2, \dots, NI$$

Physical property functions

$$H_i = H_{VL}(T_i, P_i, \bar{W}_i) \quad i = 1, 2, \dots, NI$$

$$S_i = S_{VL}(T_i, P_i, \bar{W}_i)$$

Total mole balance (with reaction)

$$\sum_{i=1}^{NI} F_i + \sum_{l=1}^{NI} R_l \left[\sum_{j=1}^{NC} V_{j,l} \right] = \sum_{i=NI+1}^{NT} F_i$$

Component mole balances (with reaction)

$$\sum_{i=1}^{NI} F_i w_{i,j} + \sum_{l=1}^{NR} V_{j,l} R_l = \sum_{i=NI+1}^{NT} F_i w_{i,j} \quad \text{for } j = 1, 2, \dots, NC$$

Molar atom balances

$$\sum_{i=1}^{NI} F_i \left[\sum_{j=1}^{NC} w_{i,j} a_{j,k} \right] = \sum_{i=NI+1}^{NT} F_i \left[\sum_{j=1}^{NC} w_{i,j} a_{j,k} \right] \quad \text{for } k = 1, 2, \dots, NE$$

Mechanical energy balance

$$\sum_{i=1}^{NI} (K_i + P_i) + \sum_{i=1}^{NI} \int_{P_{1,i}}^{P_{2,i}} V_i dp_i = \sum_{i=NI+1}^{NT} (K_i + P_i) + \sum_{i=NI+1}^{NT} \int_{P_{1,i}}^{P_{2,i}} V_i dP_i + W_{s,n} + E_{v,n}$$

Figure 31.5 Generic equations for a steady-state open system.

TABLE 31.2 Notation for Figure 13.4

$a_{j,k}$	Number of atoms of the k th chemical element in the j th component
F_i	Total flow rate of the i th stream
H_i	Relative enthalpy of the i th stream
K_j	Vaporization coefficient of the j th component
NC	Number of chemical components (compounds)
NE	Number of chemical elements
NI	Number of incoming material streams
NR	Number of chemical reactions
NT	Total number of material streams
p_i	Pressure of the i th stream
Q_n	Heat transfer for the n th process unit
R_l	Reaction expression for the l th chemical reaction
T_i	Temperature of the i th stream
$V_{j,l}$	Stoichiometric coefficient of the j th component in the l th chemical reaction
w_{ij}	Fractional composition (mass of mole) of the j th component in the i th stream
\bar{W}_i	Average composition in the i th stream
$W_{s,n}$	Work for the n th process unit
x_j	Mole fraction of component j in the liquid
y_j	Mole fraction of component j in the vapor

Equation-based codes can be formulated to include inequality constraints along with the equations. Such constraints might be of the form $a_1x_1 + a_2x_2 + \dots \leq b$, and might arise from such factors as

1. Conditions imposed in linearizing any nonlinear equations
2. Process limits for temperature, pressure, concentration
3. Requirements that variables be in a certain order
4. Requirements that variables be positive or integer

As you can see from Figures 31.4 and 31.5, if all of the equations for the material and energy balances plus the phase and chemical equilibrium relationships plus the thermodynamic and kinetic relations are all combined, they form a huge, sparse (few variables in any equation) array. The set of equations can be partitioned into subsets of equations that cannot further be decomposed, and have to be solved simultaneously. Two important aspects of solving the sets of nonlinear equations in flowsheeting codes, both equation-based and modular, are (1) the procedure for establishing the precedence order in solving the equations, and (2) the treatment of recycle (feedback) of information, material, and/or energy. Details of how to accommodate these important issues efficiently can be found in the references at the end of this chapter.

Whatever the process simulator used to solve material and energy balance problems, you must provide certain input information to the code in an acceptable format. All flowsheeting codes require that you convert the information in the flow-sheet (see Figure 31.1) and the information flowsheet as illustrated in Figure 31.3, or something equivalent. In the information flowsheet, you use the name of the mathematical model (or the subroutine in modular-based flowsheeting) that will be used for the calculations instead of the name of the process unit.

Once the information flowsheet is set up, the determination of the process topology is easy, that is, you can immediately write down the stream interconnections between the modules (or subroutines) that have to be included in the input data set. For Figure 31.3 the matrix of stream connections (the **process matrix**) is (a negative sign designates an exit stream):

Unit	Associated streams				
1	1	-2			
2	2	-3			
3	3	8	-4	-13	
4	4	7	11	-9	-5
5	5	-6			
6	6	-8	-7		
7	10	-11	-12		
8	9	-10			

b. Modular Based Process Simulators

Because plants are composed of various units operations (such as distillation, heat transfer, and so on) and unit processes (such as alkylation, hydrogenation, and so on), chemical engineers historically developed representations of each of these units or processes as self contained modules. Each module (refer to Figure 31.6) might be comprised of equations, equipment sizes, material and energy balance relations, component flow rates, and the temperatures, pressures, and phase conditions of each stream that enters and leaves the physical equipment represented by the module.

Figure 31.7 shows a flash module and the computer code that yields an output for a given input.

Values of certain parameters and variables determine the capital and operating costs for the units. Of course, the interconnections set up for the modules must be such that information can be transferred from module to module concerning the streams, compositions, flow rates, coefficients, and so on. In other words, the modules comprise a set of building blocks that can be arranged in general ways to represent any process.

The sequential modular method of flowsheeting is the one most commonly encountered in commercial computer software. A module exists for each process unit

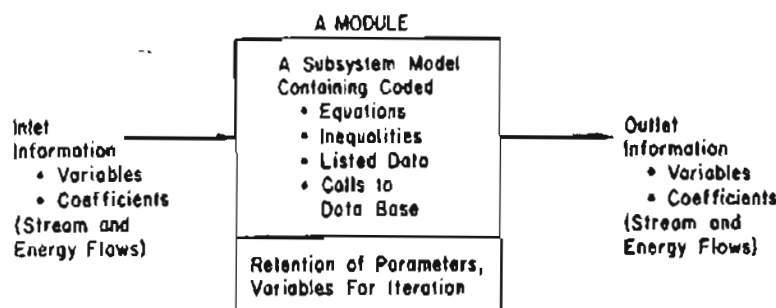


Figure 31.6 A typical process module showing the necessary interconnections of information.

in the information flowsheet. Given the values of each input stream composition, flow rate, temperature, pressure, enthalpy, and the equipment parameters, the output of a module can become the input stream to another module for which the calculations can then proceed, and so on, until the material and energy balances are resolved for the entire process. Modules are portable. By portable we mean that a subroutine corresponding to a module can be assembled as an element of a large group of subroutines, and successfully represent a certain type of equipment in any process. Figure 31.8 shows icons for typical standardized unit operations modules.

Other modules take care of equipment sizing and cost estimation, perform numerical calculations, handle recycle calculations (described in more detail below), optimize, and serve as controllers (executives for the whole set of modules so that they function in the proper sequence). Internally, a very simple module might just be a table look-up program. However, most modules consist of Fortran or C subroutines that execute a sequence of calculations. Subroutines may consist of hundreds to thousands of lines of code.

Information flows between modules via the material streams. Associated with each stream is an ordered list of numbers that characterize the stream. Table 31.3 lists a typical set of parameters associated with a stream. The presentation of the results of simulations also follows the same format as shown in Table 31.3.

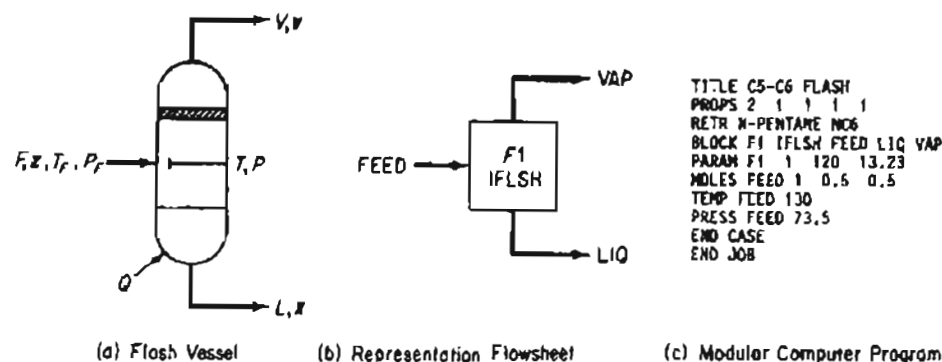


Figure 31.7 A module that represents a Flash Unit. (From J. D. Seader, W. D. Seider, and A. C. Pauls. *Flowtran Simulation-An Introduction*. CACHE, Austin, TX (1987).



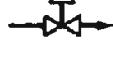
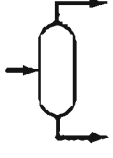
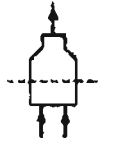


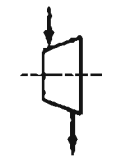
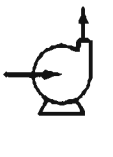
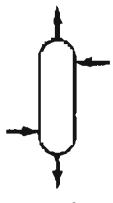
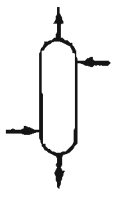
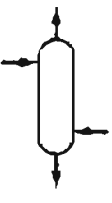

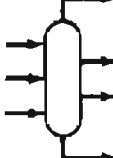
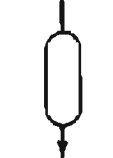
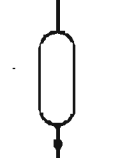
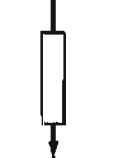
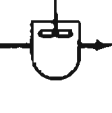
 Mixer	 Splitter	 Valve	 Flash Drum	 Furnace	 Heat Exchanger
 Compressor	 Turbine	 Process Pump	 Absorber	 Extractor	 Stripper
 Distillation Column	 Complex Column	 Simple Reactor	 Equilibrium Reactor	 Plug Flow Reactor	 C.S. Tank Reactor

Figure 31.8 Typical process modules used in sequential modular-based flow-sheeting codes with their subroutine names.

As a user of a modular-based code, you have to provide

1. The process topology
2. Input stream information including physical properties and connections
3. Design parameters needed in the modules and equipment specifications
4. Convergence criteria

TABLE 31.3 Stream Parameters

1. Stream number*
2. Stream flag (designates type of stream)
3. Total flow, lb mol/hr
4. Temperature, °F
5. Pressure, psia
6. Flow of component 1, lb mol/hr
7. Flow of component 2, lb mol/hr
8. Flow of component 3, lb mol/hr
9. Molecular weight
10. Vapor fraction
11. Enthalpy
12. Sensitivity

*Corresponds to an arbitrary numbering scheme used on the information flowsheet.

In addition, you sometimes may have to insert a preferred calculation order for the modules. When economic evaluation and optimization are being carried out, you must also provide cost data and optimization criteria.

Modular-based flowsheeting exhibits several advantages in design. The flow-sheet architecture is easily understood because it closely follows the process flow-sheet. Individual modules can easily be added and removed from the computer package. Furthermore, new modules may be added to or removed from the flowsheet without affecting other modules. Modules at two different levels of accuracy can be substituted for one another.

Modular-based flowsheeting also has certain drawbacks:

1. The output of one module is input to another. The input and output variables in a computer module are fixed so that you cannot arbitrarily introduce an output and generate an input as sometimes can be done in an equation-based code.
2. The modules require extra computer time to generate reasonably accurate derivatives or their substitutes, especially if a module contains tables, functions with discrete variables, discontinuities, and so on. Perturbation of the input to a module is the primary way in which a finite-difference substitute for a derivative can be generated.
3. The modules may require a fixed precedence order of solution, that is, the output of one module must become the input of another; hence convergence may be slower than in an equation-solving method, and the computational costs may be high.
4. To specify a parameter in a module as a decision variable in the design of a plant, you have to place a control block around the module and adjust the parameter such that design specifications are met. This arrangement creates a loop. If the values of many design variables are to be determined, you might end up with several nested loops of calculation (which do, however, enhance stability). A similar arrangement must be used if you want to impose constraints.
5. Conditions imposed on a process (or a set of equations for that matter) may cause the unit physical states to move from two-phase to single-phase operation, or the reverse. (This situation is true of equation based codes as well.) You have to foresee and accommodate such changes in state.

An engineer can usually carry out the partitioning and nesting, and determine the computational sequence for a flowsheet by inspection if the flowsheet is not too complicated. In some codes, the user supplies the computational sequence as input. Other codes determine the sequence automatically. In ASPEN, for example, the code is capable of determining the entire computational sequence, but the user can supply as many specifications as desired, up to and including the complete computational sequence. Consult one of the supplementary references at the end of this chap-

ter for detailed information on optimal techniques of using simulator techniques beyond our scope in this text.

Once the sequence of calculations codes is specified, everything is in order for the solution of material and energy balances. All that has to be done is to calculate the correct values for the stream flow rates and their properties. To execute the calculations, various numerical algorithms can be selected by the user or determined by the simulator. The results can be displayed as tables, graphs, charts, etc.

Looking Back

In this chapter we described the two main ways of solving the material and energy balances in process simulators: using (a) equation-based, and (b) modular-based computer software.

Discussion Question

1. A number of articles have been written of the subject of "paper vs. polystyrene" as materials for paper cups. Set up the flowsheets for the production of each, and include all of the quantitative and qualitative factors, both positive and negative, for the production from basic raw materials to the final product. Indicate what material and energy balances are needed, and, if possible, collect data so that they can be solved. Summarize the material and energy usage in the manufacture of a cup.

SUPPLEMENTARY REFERENCES

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Web Sites

The best site by far is

<http://www.interduct.tudelft.nl/Pltools/news/news.html>

Other sites are

<http://www.aeat.co.uk/pes/axsys/features.htm>

http://www.capec.kt.dtu.dk/capec/docs/main/36445/Lecture_Notes.htm

http://www.fantoft.com/FPT/Business_Areas/process_simulators/simulat_main.htm

<http://members.ozemail.com.au/~wadsley/models.html>

http://www.protodesign_in.com

<http://www.umsl.edu/~chemist/books/softpubs.html>

<http://www.virtualmaterials.com/courses.html>

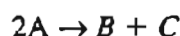
Each vendor listed in Table 31.1 has a web site that contains considerable information and demos pertaining to their particular software.

PROBLEMS

- 31.1** In petroleum refining, lubricating oil is treated with sulfuric acid to remove unsaturated compounds, and after settling, the oil and acid layers are separated. The acid layer is added to water and heated to separate the sulfuric acid from the sludge con-

tained in it. The dilute sulfuric acid, now 20% H_2SO_4 at 82°C , is fed to a Simonson-Mantius evaporator, which is supplied with saturated steam at 400 kPa gauge to lead coils submerged in the acid, and the condensate leaves at the saturation temperature. A vacuum is maintained at 4.0 kPa by means of a barometric leg. The acid is concentrated to 80% H_2SO_4 ; the boiling point at 4.0 kPa is 121°C . How many kilograms of acid can be concentrated per 1000 kg of steam condensed?

- 31.2** You are asked to perform a feasibility study on a continuous stirred tank reactor shown in Figure P31.2 (which is presently idle) to determine if it can be used for the second-order reaction



Since the reaction is exothermic, a cooling jacket will be used to control the reactor temperature. The total amount of heat transfer may be calculated from an overall heat transfer coefficient (U) by the equation

$$\dot{Q} = UA \Delta T$$

where \dot{Q} = total rate of heat transfer from the reactants to the water jacket in the steady state

U = empirical coefficient

A = area of transfer

ΔT = temperature difference (here $T_1 - T_2$)

Some of the energy released by the reaction will appear as sensible heat in stream F_2 , and some concern exists as to whether the fixed flow rates will be sufficient to keep the fluids from boiling while still obtaining good conversion. Feed data is as follows:

Component	Feed rate (lb mol/hr)	C_p [Btu/(lb mol)($^\circ\text{F}$)]	MW
A	214.58	41.4	46
B	23.0	68.4	76
C	0.0	4.4	16

The consumption rate of A may be expressed as

$$-2k(C_A)^2V_R$$

where

$$C_A = \frac{(F_{1,A})(\rho)}{\sum(F_{1,i})(MW_i)} = \text{concentration of A, lb mol/ft}^3$$

$$k = k_0 \exp\left(\frac{-E}{RT}\right)$$

k_0 , E , R are constants and T is the absolute temperature.

Solve for the temperatures of the exit streams and the product composition of the steady-state reactor using the following data:

Fixed parameters

$$\begin{aligned}\text{Reactor volume} &= V_R = 13.3 \text{ ft}^3 \\ \text{Heat transfer area} &= A = 29.9 \text{ ft}^2 \\ \text{Heat transfer coefficient} &= U = 74.5 \text{ Btu}/(\text{hr})(\text{ft}^2)(^\circ\text{F})\end{aligned}$$

Variable input

$$\begin{aligned}\text{Reactant feed rate} &= F_1 \text{ (see table above)} \\ \text{Reactant feed temperature} &= T_1 = 80^\circ\text{F} \\ \text{Water feed rate} &= F_3 = 247.7 \text{ lb mol/hr water} \\ \text{Water feed temperature} &= T_3 = 75^\circ\text{F}\end{aligned}$$

Physical and thermodynamic data

$$\begin{aligned}\text{Reaction rate constant} &= k_0 = 34 \text{ ft}^3/(\text{lb mol})/(\text{hr}) \\ \text{Activation energy/gas constant} &= E/R = 1000^\circ\text{R}\end{aligned}$$

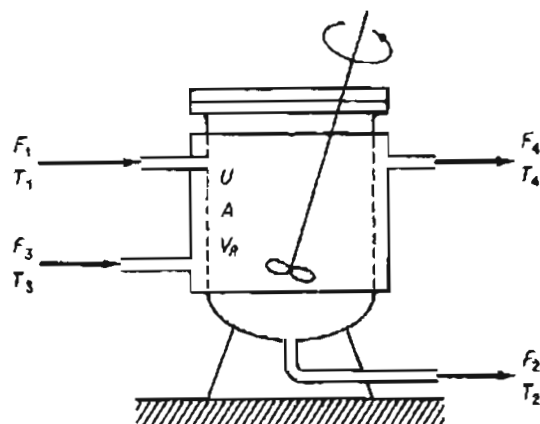


Figure P31.2

$$\begin{aligned}\text{Heat of reaction} &= \Delta H = -5000 \text{ btu/lb mol } A \\ \text{Heat capacity of water} &= C_{pw} = 18 \text{ Btu}/(\text{lb mol})(^\circ\text{F}) \\ \text{Product component density} &= \rho = 55 \text{ lb/ft}^3\end{aligned}$$

The densities of each of the product components are essentially the same. Assume that the reactor contents are perfectly mixed as well as the water in the jacket, and that the respective exit stream temperatures are the same as the reactor contents or jacket contents.

- 31.3** The stream flows for a plant are shown in Figure P31.3. Write the material and energy balances for the system and calculate the unknown quantities in the diagram (A to F). There are two main levels of steam flow: 600 psig and 50 psig. Use the steam tables for the enthalpies.
- 31.4** Figure P31.4 shows a calciner and the process data. The fuel is natural gas. How can the energy efficiency of this process be improved by process modification? Suggest at least two ways based on the assumption that the supply conditions of the air and fuel remain fixed (but these streams can be possibly passed through heat exchangers). Show all calculations.

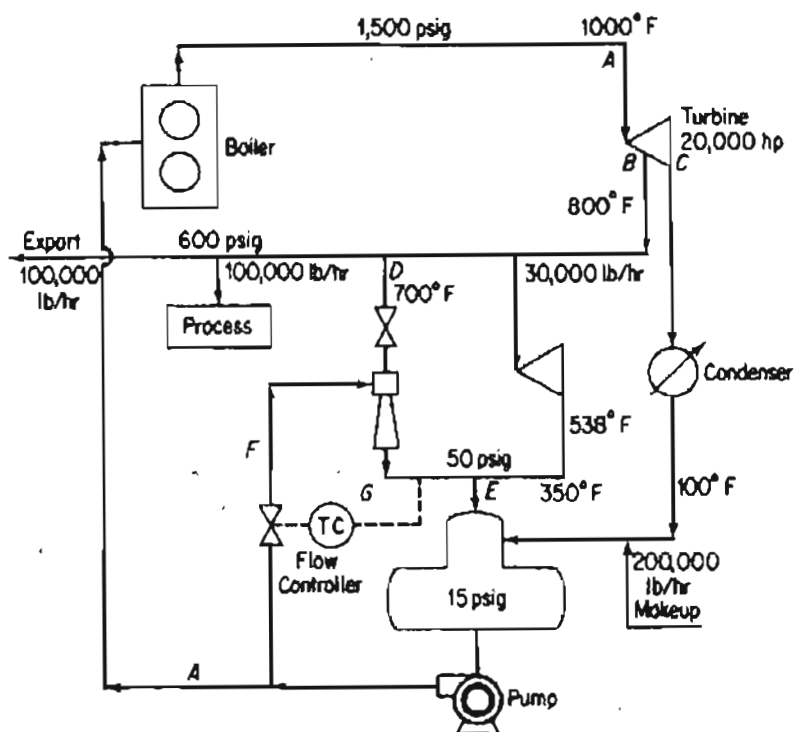


Figure P31.3

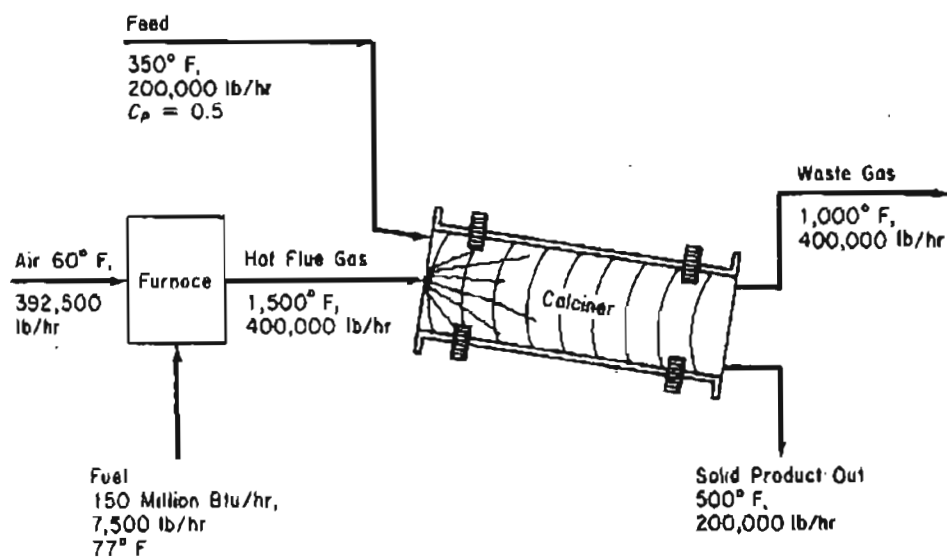


Figure P31.4

- 31.5** Limestone (CaCO_3) is converted into CaO in a continuous vertical kiln (see Figure P31.5). Heat is supplied by combustion of natural gas (CH_4) in direct contact with the limestone using 50% excess air. Determine the kilograms of CaCO_3 that can be processed per kilogram of natural gas. Assume that the following average heat capacities apply:

$$C_p \text{ of } \text{CaCO}_3 = 234 \text{ J/(g mol)}(^{\circ}\text{C})$$

$$C_p \text{ of } \text{CaO} = 111 \text{ J/(g mol)}(^{\circ}\text{C})$$

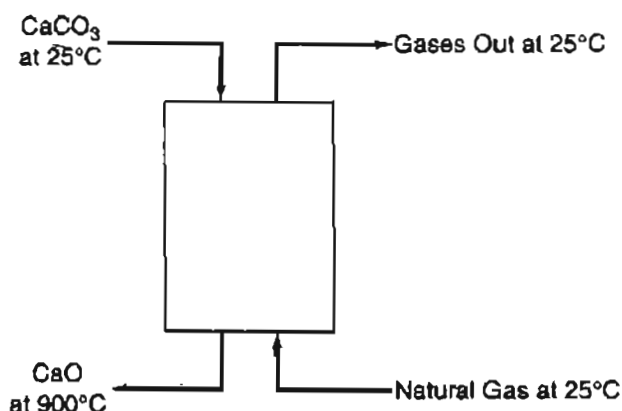


Figure P31.5

- 31.6** A feed stream of 16,000 lb/hr of 7% by weight NaCl solution is concentrated to a 40% by weight solution in an evaporator. The feed enters the evaporator, where it is heated to 180°F. The water vapor from the solution and the concentrated solution leave at 180°F. Steam at the rate of 15,000 lb/hr enters at 230°F and leaves as condensate at 230°F. See Figure P31.6.

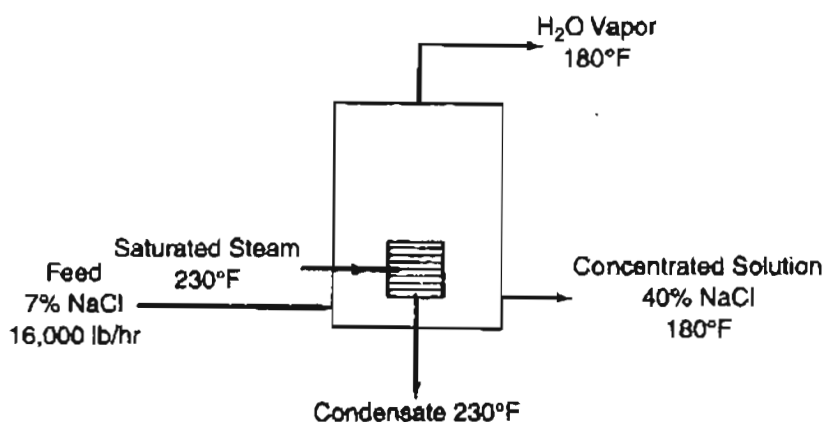


Figure P31.6

- (a) What is the temperature of the feed as it enters the evaporator?
 (b) What weight of 40% NaCl is produced per hour?

Assume that the following data apply:

Average C_p 7% NaCl soln: 0.92 Btu/(lb)(°F)

Average C_p 40% NaCl soln: 0.85 Btu/(lb)(°F)

$\Delta \hat{H}_{\text{vap}}$ of H₂O at 180°F = 990 Btu/lb

$\Delta \hat{H}_{\text{vap}}$ of H₂O at 230°F = 959 Btu/lb

- 31.7** The Blue Ribbon Sour Mash Company plans to make commercial alcohol by a process shown in Figure P31.7. Grain mash is fed through a heat exchanger where it is heated to 170°F. The alcohol is removed as 60% by weight alcohol from the first

fractionating column; the bottoms contain no alcohol. The 60% alcohol is further fractionated to 95% alcohol and essentially pure water in the second column. Both stills operate at a 3:1 reflux ratio and heat is supplied to the bottom of the columns by steam. Condenser water is obtainable at 80°F. The operating data and physical properties of the streams have been accumulated and are listed for convenience:

Stream	State	Boiling point (°F)	C_p [Btu/(lb)(°F)]		Heat of vaporization (Btu/lb)
			Liquid	Vapor	
Feed	Liquid	170	0.96	—	950
60% alcohol	Liquid or vapor	176	0.85	0.56	675
Bottoms I	Liquid	212	1.00	0.50	970
95% alcohol	Liquid or vapor	172	0.72	0.48	650
Bottoms II	Liquid	212	1.0	0.50	970

Prepare the material balances for the process, calculate the precedence order for solution, and

- Determine the weight of the following streams per hour:
 - Overhead product, column I
 - Reflux, column I
 - Bottoms, column I
 - Overhead product, column II
 - Reflux, column II
 - Bottoms, column II
- Calculate the temperature of the bottoms leaving heat exchanger III.
- Determine the total heat input to the system in Btu/hr.

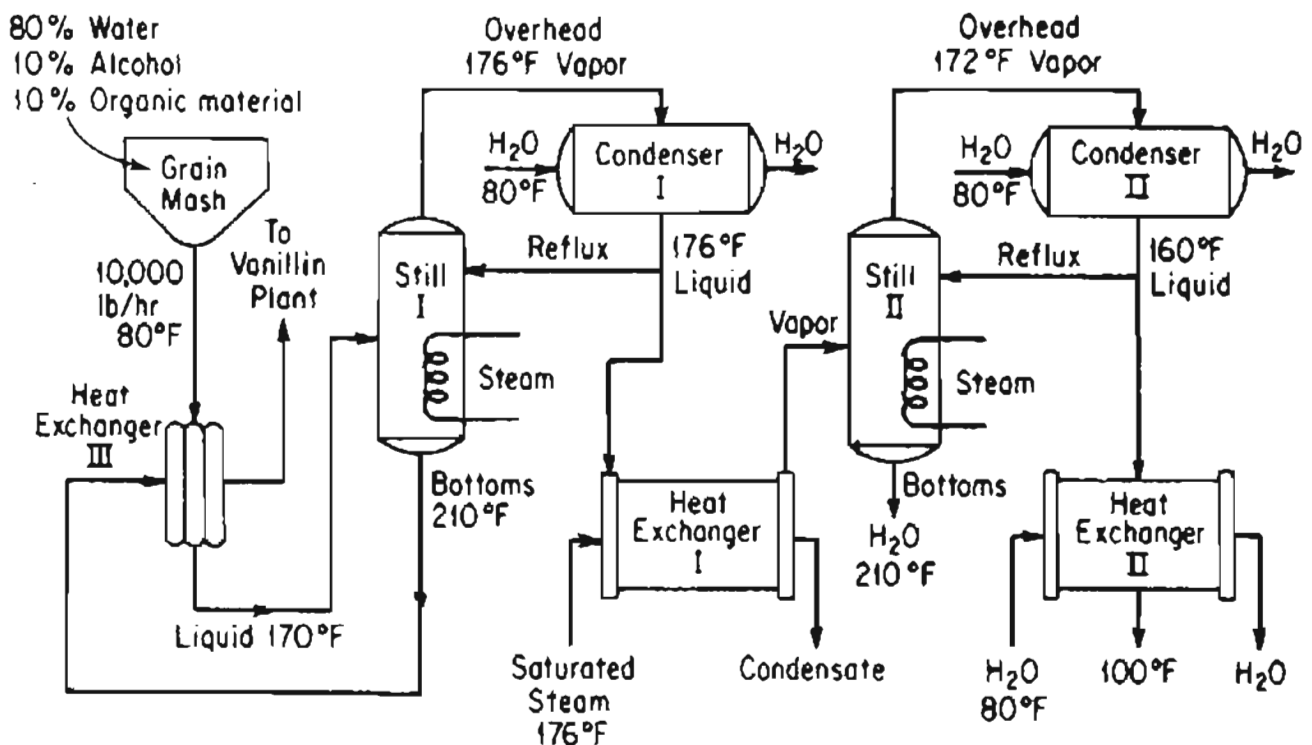


Figure P31.7

- (d) Calculate the water requirements for each condenser and heat exchanger II in gal/hr if the maximum exit temperature of water from this equipment is 130°F.

31.8 Toluene, manufactured by the conversion of *n*-heptane with a Cr_2O_3 -on- Al_2O_3 catalyst



by the method of hydroforming, is recovered by use of a solvent. See Figure P31.8 for the process and conditions.

The yield of toluene is 15 mole % based on the *n*-heptane charged to the reactor. Assume that 10 kg of solvent are used per kilogram of toluene in the extractors.

- Calculate how much heat has to be added or removed from the catalytic reactor to make it isothermal at 425°C.
- Find the temperature of the *n*-heptane and solvent stream leaving the mixer-settlers if both streams are at the same temperature.
- Find the temperature of the solvent stream after it leaves the heat exchanger.
- Calculate the heat duty of the fractionating column in kJ/kg of *n*-heptane feed to the process.

	$-\Delta H_f^\circ$ (kJ/g mol)	C_p [J/(g)(°C)]		$\Delta H_{\text{vaporization}}$ (kJ/kg)	Boiling point (K)
		Liquid	Vapor		
Toluene ^b	12.00	2.22	2.30	364	383.8
<i>n</i> -Heptane	-224.4	2.13	1.88	318	371.6
Solvent	—	1.67	2.51	—	434

^aAs liquids.

^bThe heat of solution of toluene in the solvent is -23 J/g toluene.

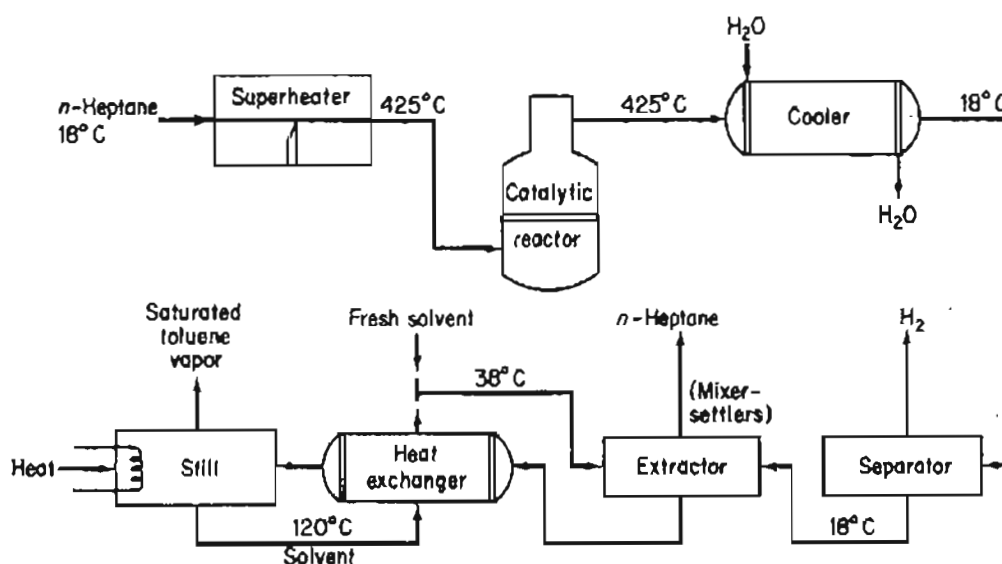


Figure P31.8

- 31.9 One hundred thousand pounds of a mixture of 50% benzene, 40% toluene, and 10% *o*-xylene is separated every day in a distillation-fractionation plant as shown on the flowsheet for Figure P31.9.

	Boiling point (°C)	C_p liquid [cal/(g)(°C)]	Latent heat of vap. (cal/g)	C_p vapor [cal/(g)(°C)]
Benzene	80	0.44	94.2	0.28
Toluene	109	0.48	86.5	0.30
<i>o</i> -Xylene	143	0.48	81.0	0.32
Charge	90	0.46	88.0	0.29
Overhead T_I	80	0.45	93.2	0.285
Residue T_I	120	0.48	83.0	0.31
Residue T_{II}	413	0.48	81.5	0.32

The reflux ratio for tower I is 6:1; the reflux ratio for tower II is 4:1; the charge to tower I is liquid; the chart to tower II is liquid. Compute:

- The temperature of the mixture at the outlet of the heat exchanger (marked as T^*)
 - The Btu supplied by the steam reboiler in each column
 - The quantity of cooling water required in gallons per day for the whole plant
 - The energy balance around tower I
- 31.10 Sulfur dioxide emissions from coal-burning power plants causes serious atmospheric pollution in the eastern and midwestern portions of the United States. Unfortunately, the supply of low-sulfur coal is insufficient to meet the demand. Processes presently under consideration to alleviate the situation include coal gasification followed by desulfurization and stack-gas cleaning. One of the more promising stack-gas-cleaning processes involves reacting SO_2 and O_2 in the stack gas with a solid metal oxide sorbent to give the metal sulfate, and then thermally regenerating the sorbent and absorbing the result SO_3 to produce sulfuric acid. Recent laboratory experiments indicate that sorption and regeneration can be carried out with several metal oxides, but no pilot or full-scale processes have yet been put into operation.

You are asked to provide a preliminary design for a process that will remove 95% of the SO_2 from the stack gas of a 1000-MW power plant. Some data are given below and in the flow diagram of the process (Figure P31.10). The sorbent consists of fine particles of a dispersion of 30% by weight CuO in a matrix of inert porous Al_2O_3 . This solid reacts in the fluidized-bed absorber at 315°C . Exit solid is sent to the regenerator, where SO_3 is evolved at 700°C , converting the CuSO_4 present back to CuO . The fractional conversion of CuO to CuSO_4 that occurs in the sorber is called α and is an important design variable. You are asked to carry out your calculations for $\alpha = 0.2, 0.5$, and 0.8 . The SO_3 produced in the regenerator is swept out by recirculating air. The SO_3 -laden air is sent to the acid tower, where the SO_3 is absorbed in recirculating sulfuric acid and oleum, part of which is withdrawn as salable byproducts. You will notice that the sorber, regenerator, and perhaps the acid tower are adiabatic; their temperatures are adjusted by heat exchange with incoming

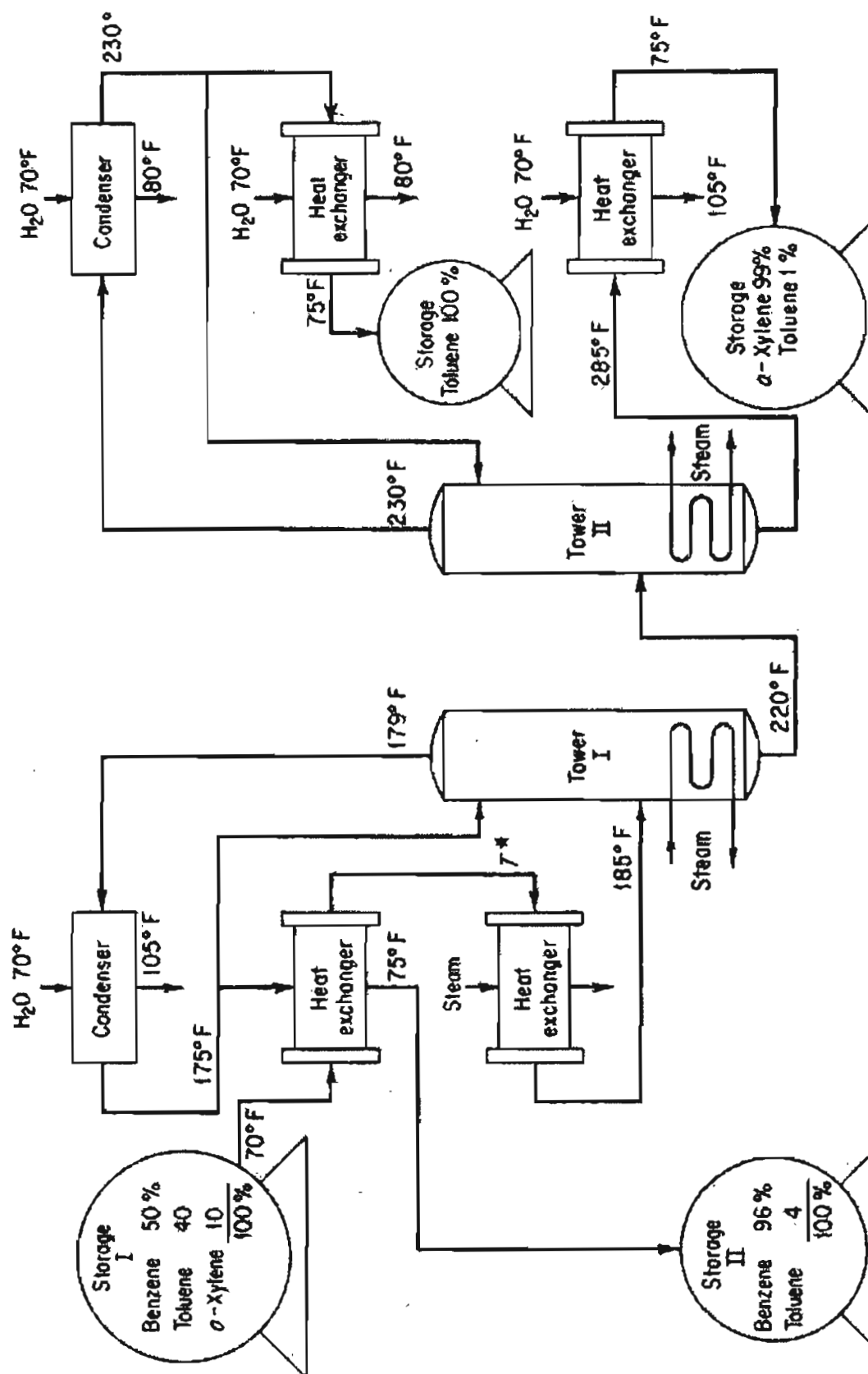


Figure P31.9

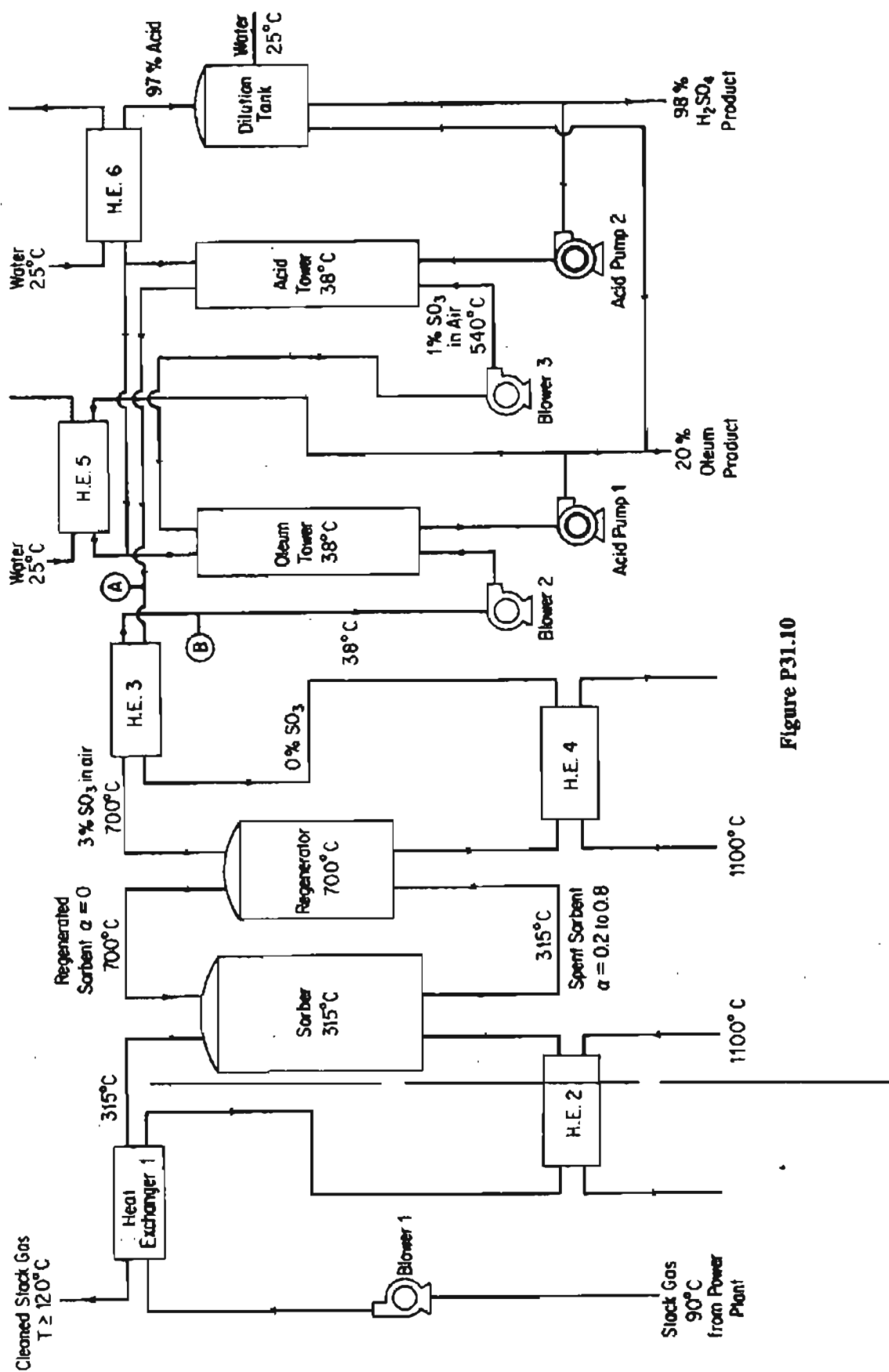


Figure P31.10

streams. Some of the heat exchangers (nos. 1 and 3) recover heat by countercurrent exchange between the feed and exit streams. Additional heat is provided by withdrawing flue gas from the power plant at any desired high temperature up to 1100°C and then returning it at a lower temperature. Cooling is provided by water at 25°C. As a general rule, the temperature difference across heat-exchanger walls separating the two streams should average about 28°C. The nominal operating pressure of the whole process is 10 kPa. The three blowers provide 6 kPa additional head for the pressure losses in the equipment, and the acid pumps have a discharge pressure of 90 kPa gauge. You are asked to write the material and energy balances and some equipment specifications as follows:

- Sorber, regenerator, and acid tower. Determine the flow rate, composition, and temperature of all streams entering and leaving.
- Heat exchangers. Determine the heat load, and flow rates, temperatures, and enthalpies of all streams.
- Blowers. Determine the flow rate and theoretical horsepower.
- Acid pump. Determine the flow rate and theoretical horsepower.

Use SI units. Also, use a basis of 100 kg of coal burned for all your calculations; then convert to the operating basis at the end of the calculations.

Power plant operation. The power plant burns 340 metric tons/hr of coal having the analysis given below. The coal is burned with 18% excess air, based on complete combustion to CO₂, H₂O, and SO₂. In the combustion only the ash and nitrogen are left unburned; all the ash has been removed from the stack gas.

Element	Wt. %
C	76.6
H	5.2
O	6.2
S	2.3
N	1.6
Ash	8.1

Data on Solids (Units of C_p are J/(g mol)(K); units of H are kJ/g mol.)

$T(K)$	Al_2O_3		CuO		$CuSO_4$	
	C_p	$H_T - H_{298}$	C_p	$H_T - H_{298}$	C_p	$H_T - H_{298}$
298	79.04	0.00	42.13	0.00	98.9	0.00
400	96.19	9.00	47.03	4.56	114.9	10.92
500	106.10	19.16	50.04	9.41	127.2	23.05
600	112.5	30.08	52.30	14.56	136.3	36.23
700	117.0	41.59	54.31	19.87	142.9	50.25
800	120.3	53.47	56.19	25.40	147.7	64.77
900	122.8	65.65	58.03	31.13	151.0	79.71
1000	124.7	77.99	59.87	37.03	153.8	94.98

31.11 When coal is distilled by heating without contact with air, a wide variety of solid, liquid, and gaseous products of commercial importance are produced, as well as some significant air pollutants. The nature and amounts of the products produced depend on the temperature used in the decomposition and the type of coal. At low temperatures (400 to 750°C) the yield of synthetic gas is small relative to the yield of liquid products, whereas at high temperatures (above 900°C) the reverse is true. For the typical process flowsheet, shown in Figure P31.11.

- How many tons of the various products are being produced?
- Make an energy balance around the primary distillation tower and benzol tower.
- How much (in pounds) of 40% NaOH solution is used per day for the purification of the phenol?
- How much 50% H_2SO_4 is used per day in the pyridine purification?
- What weight of Na_2SO_4 is produced per day by the plant?
- How many cubic feet of gas per day are produced? What percent of the gas (volume) is needed for the ovens?

Products Produced Per Ton of Coal Charged	Mean C_p Liquid (cal/g)	Mean C_p Vapor (cal/g)	Mean C_p Solid (cal/g)	Melting Point (°C)	Boiling Point (°C)
Synthetic gas—10,000 ft ³ (555 Btu/ft ³)					
(NH_4) ₂ SO ₄ , 22 lb					
Benzol, 15 lb	0.50	0.30	—	—	60
Toluol, 5 lb	0.53	0.35	—	—	109.6
Pyridine, 3 lb	0.41	0.28	—	—	114.1
Phenol, 5 lb	0.56	0.45	—	—	182.2
Naphthalene, 7 lb	0.40	0.35	0.281 + 0.00111 $T_{\text{°F}}$	80.2	218
Cresols, 20 lb	0.55	0.50	—	—	202
Pitch, 40 lb	0.65	0.60	—	—	400
Coke, 1500 lb	—	—	0.35	—	—

	ΔH_{vap} (cal/g)	ΔH_{fusion} (cal/g)
Benzol	97.5	—
Toluol	86.53	—
Pyridine	107.36	—
Phenol	90.0	—
Naphthalene	75.5	35.6
Cresols	100.6	—
Pitch	120	—

31.12 A gas consisting of 95 mol % hydrogen and 5 mol % methane at 100°F and 30 psia is to be compressed to 569 psia at a rate of 440 lb mol/hr. A two-stage compressor system has been proposed with intermediate cooling of the gas to 100°F via a heat exchanger. See Figure P31.12. The pressure drop in the heat exchanger from the inlet

stream (S1) to the exit stream (S2) is 2.0 psia. Using a process simulator program, analyze all of the steam parameters subject to the following constraints: The exit stream from the first stage is 100 psia; both compressors are positive-displacement type and have a mechanical efficiency of 0.8, a polytropic efficiency of 1.2, and a clearance fraction of 0.05.

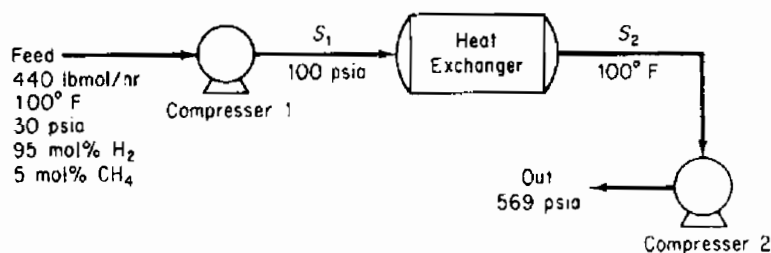


Figure P31.12

- 31.13** A gas feed mixture at 85°C and 100 psia having the composition shown in Figure P31.13 is flashed to separate the majority of the light from the heavy components. The flash chamber operates at 5°C and 25 psia. To improve the separation process, it has been suggested to introduce a recycle as shown in Figure P31.13. Will a significant improvement be made by adding a 25% recycle of the bottoms? 50%? With the aid of a computer process simulator, determine the molar flow rates of the streams for each of the three cases.

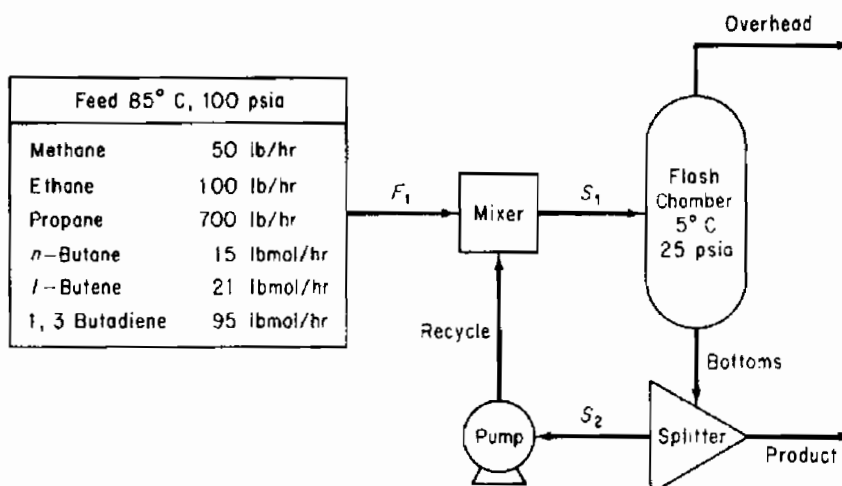


Figure P31.13

- 31.14** A mixture of three petroleum fractions containing lightweight hydrocarbons is to be purified and recycled back to a process. Each of the fractions is denoted by its normal boiling point: BP135, BP260, and BP500. The gases separated from this feed are to be compressed as shown in Figure P31.14. The inlet feed stream (1) is at 45°C and 450 kPa, and has the composition shown. The exit gas (10) is compressed to 6200 kPa by a three-stage compressor process with intercooling of the vapor streams to 60°C by passing through a heat exchanger. The exit pressure for compressor 1 is 1100 kPa and 2600 kPa for compressor 2. The efficiencies for compressors 1, 2,

and 3, with reference to an adiabatic compression are, 78, 75, and 72%, respectively. Any liquid fraction drawn off from a separator is recycled to the previous stage. Estimate the heat duty (in kJ/hr) of the heat exchangers and the various stream compositions (in kg mol/hr) for the system. Note that the separators may be considered as adiabatic flash tanks in which the pressure decrease is zero. This problem has been formulated from *Application Briefs of Process*, the user manual for the computer simulation software package of Simulation Science, Inc.

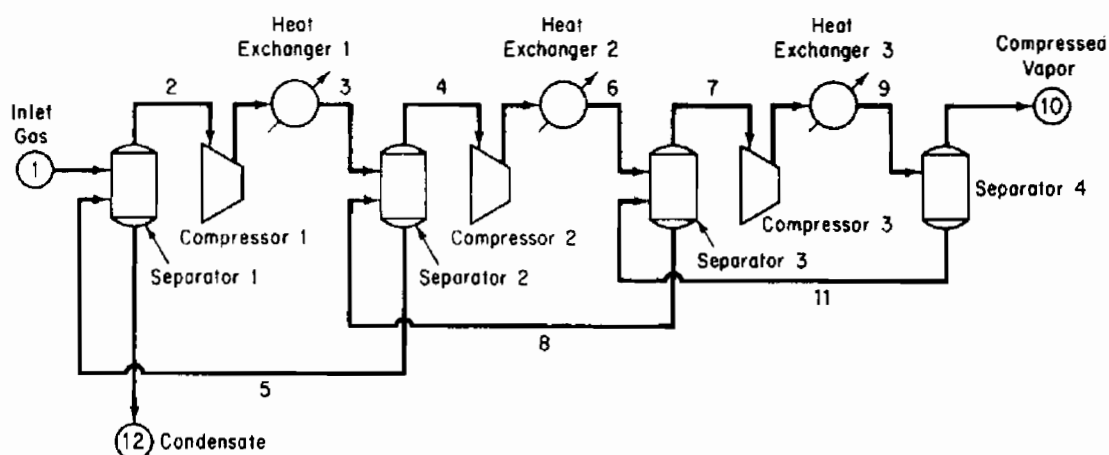


Figure P31.14

Component	kg mol/hr	M.W.	sp gr	Normal boiling point (°C)
Nitrogen	181			
Carbon dioxide	1,920			
Methane	14,515			
Ethane	9,072			
Propane	7,260			
Isobutane	770			
<i>n</i> -Butane	2,810			
Isopentane	953			
<i>n</i> -Pentane	1,633			
Hexane	1,542			
BP135	11,975	120	0.757	135
BP260	9,072	200	0.836	260
BP500	9,072	500	0.950	500

- 31.15** A demethanizer tower is used in a refinery to separate natural gas from a light hydrocarbon gas mixture stream (1) having the composition listed below. However, initial calculations show that there is considerable energy wastage in the process. A proposed improved system is outlined in Figure P31.15. Calculate the temperature (°F), pressure (psig), and composition (lb mol/hr) of all the process streams in the proposed system.

Inlet gas at 120°F and 588 psig, stream (1), is cooled in the tube side of a gas-gas heat exchanger by passing the tower overhead, stream (8), through the shell side. The temperature difference between the exit streams (2) and (10) of the heat ex-

changer is to be 10°F . Note that the pressure drop through the tube side is 10 psia and 5 psia on the shell side. The feed stream (2) is then passed through a chiller in which the temperature drops to -84°F and a pressure loss of 5 psi results. An adiabatic flash separator is used to separate the partially condensed vapor from the remaining gas. The vapor then passes through an expander turbine and is fed to the first tray of the tower at 125 psig. The liquid stream (5) is passed through a valve, reducing the pressure to that of the third tray on the lower side. The expander transfers 90% of its energy output to the compressor. The efficiency with respect to an adiabatic compression is 80% for the expander and 75% for the compressor. The process requirements are such that the methane-to-ethane ratio in the demethanizer liquids in stream (9) is to be 0.015 by volume; the heat duty on the reboiler is variable to achieve this ratio. A process rate of 23.06×10^6 standard cubic feet per day of feed stream (1) is required.

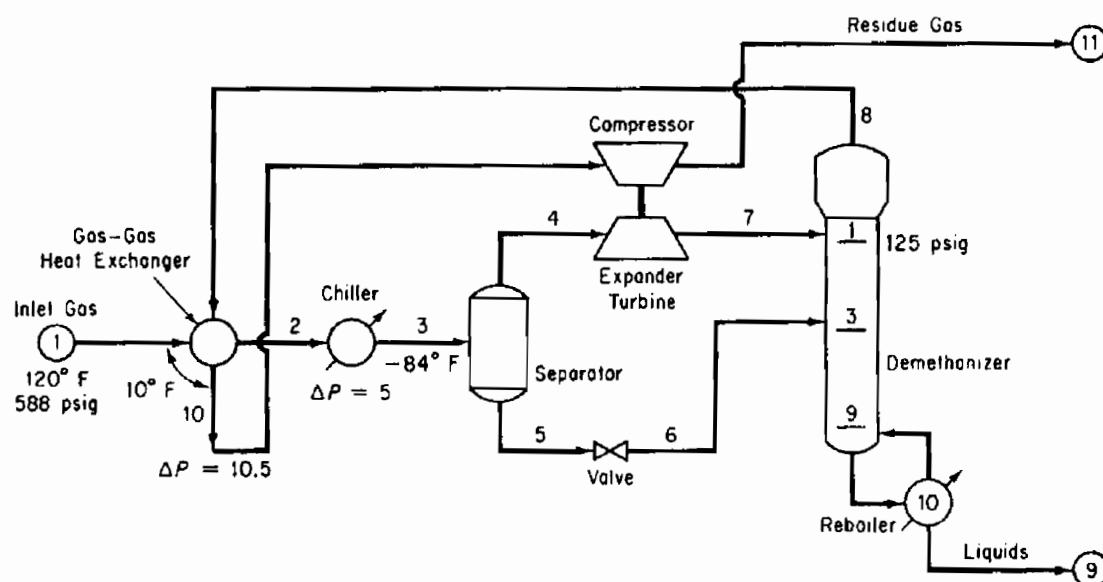


Figure P31.15

Component	Mol %
Nitrogen	7.91
Methane	73.05
Ethane	7.68
Propane	5.69
Isopropane	0.99
<i>n</i> -butane	2.44
Isopentane	0.69
<i>n</i> -pentane	0.82
C ₆	0.42
C ₇	0.31
Total	100.00

The tower has 10 trays, including the reboiler. *Note:* To reduce the number of trials, the composition of stream (3) may be referenced to stream (1), and if the exit stream

of the chiller is given a dummy symbol, the calculations sequence can begin at the separator, thus eliminating the recycle loop.

Carry out the solution of the material and energy balances for the flowsheet in Figure P31.15, determine the component and total mole flows, and determine the enthalpy flows for each stream. Also find the heat duty of each heat exchanger.

This problem has been formulated from *Application Briefs of Process*, the user manual for the computer simulation software package of Simulation Sciences, Inc.

31.16 Determine the values of the unknown quantities in Figure P31.16 by solving the following set of linear material and energy balances that represent the steam balance:

(a) $181.60 - x_3 - 132.57 - x_4 - x_5 = -y_1 - y_2 + y_5 + y_4 = 5.1$

(b) $1.17x_3 - x_6 = 0$

(c) $132.57 - 0.745x_7 = 61.2$

(d) $x_5 + x_7 - x_8 - x_9 - x_{10} + x_5 = y_7 + y_8 = y_3 = 99.1$

(e) $x_8 + x_9 + x_{10} + x_{11} - x_{12} - x_{13} = -y_7 = -8.4$

(f) $x_6 - x_{15} = y_{12} = y_5 = 24.2$

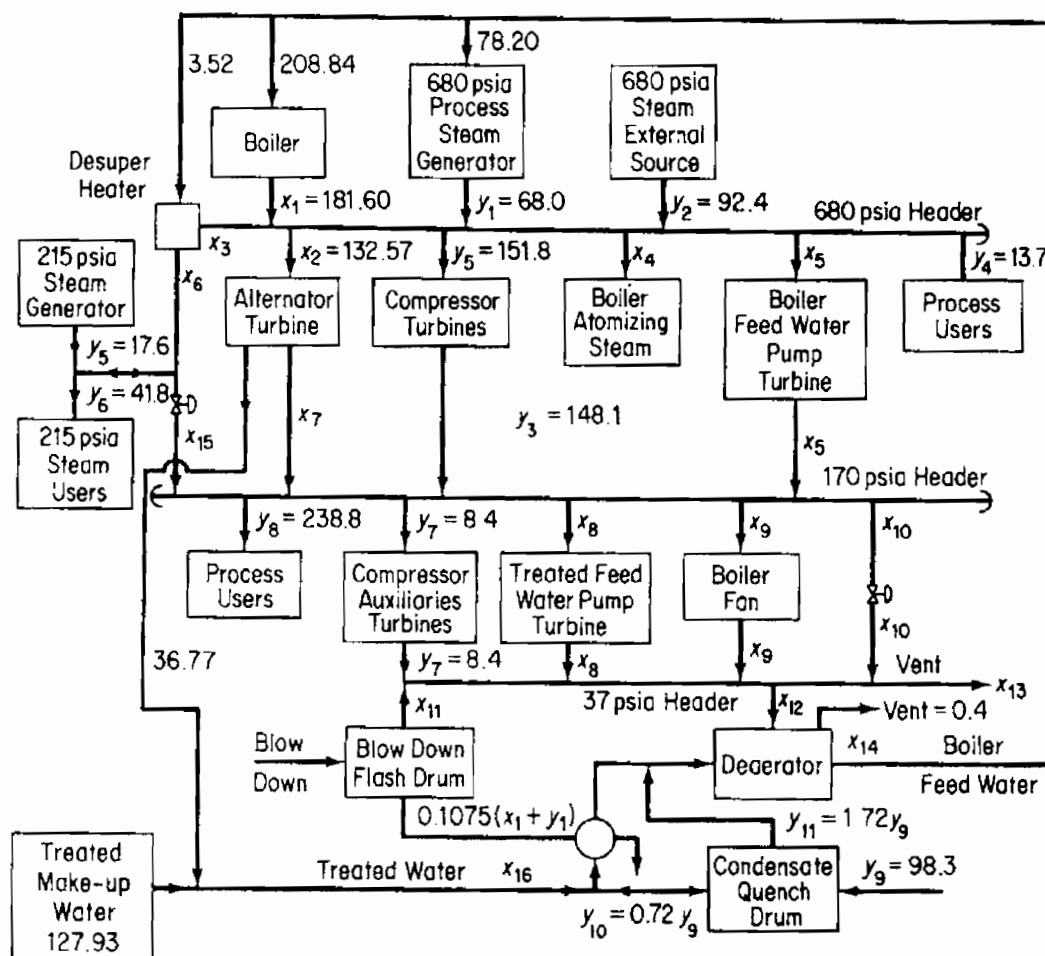


Figure P31.16

$$(g) -1.15(181.60) + x_3 - x_6 + x_{12} + x_{16} = 1.15y_1 - y_9 + 0.4 = -19.7$$

$$(h) 181.60 - 4.594x_{12} - 0.11x_{16} = -y_1 + 1.0235y_9 + 2.45 = 35.05$$

$$(i) -0.0423(181.60) + x_{11} = 0.0423y_1 = 2.88$$

$$(j) -0.016(181.60) + x_4 = 0$$

$$(k) x_8 - 0.0147x_{16} = 0$$

$$(l) x_5 - 0.07x_{14} = 0$$

$$(m) -0.0805(181.60) + x_9 = 0$$

$$(n) x_{12} - x_{14} + x_{16} = 0.4 - y_9 = -97.9$$

There are four levels of steam: 680, 215, 170, and 37 psia. The 14 x_i , $i = 3, \dots, 16$, are the unknowns and the y_i are given parameters for the system. Both x_i and y_i have the units of 10^3 lb/hr.

CHAPTER 32

UNSTEADY-STATE MATERIAL AND ENERGY BALANCES

Unsteady-state problems in previous chapters have used the overall or integrated accumulation term in the material and energy balances. Now we focus our attention briefly on **unsteady-state** processes in which the value of the state (dependent variable) as a function of time is of interest. Recall that the term unsteady state refers to processes in which quantities or operating conditions within the system *change with time*. Sometimes you will hear the word *transient state* applied to such processes. The unsteady state is somewhat more complicated than the steady state, and, in general, problems involving unsteady-state processes are somewhat more difficult to formulate and solve than those involving steady-state processes. However, a wide variety of important industrial problems fall into this category, such as the startup of equipment, batch heating or reactions, the change from one set of operating conditions to another, and the perturbations that develop as process conditions fluctuate.

Your objectives in studying this chapter are to be able to:

1. Write down the macroscopic unsteady-state material and energy balances in words and in symbols.
2. Solve simple ordinary differential material or energy balance equations given the initial conditions.
3. Take a word problem and translate it into a differential equation(s).

Looking Ahead

In this section we describe how lumped macroscopic material and energy balances are developed for unsteady-state processes in which time is the independent variable.

The macroscopic balance ignores all the detail within a system and consequently results in a balance about the entire system. Time is the independent variable in the balance. The dependent variables, such as concentration and temperature, are not functions of position but represent overall averages throughout the entire volume of the system. In effect, the system is assumed to be sufficiently well mixed so that the output concentrations and temperatures are equivalent to the concentrations and temperatures inside the system.

To assist in the translation of Eq. (32.1)

$$\left\{ \begin{array}{c} \text{accumulation} \\ \text{or depletion} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{c} \text{transport into} \\ \text{system through} \\ \text{system} \\ \text{boundary} \end{array} \right\} - \left\{ \begin{array}{c} \text{transport out} \\ \text{of system} \\ \text{through system} \\ \text{boundary} \end{array} \right\} + \left\{ \begin{array}{c} \text{generation} \\ \text{within} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{c} \text{consumption} \\ \text{within} \\ \text{system} \end{array} \right\} \quad (32.1)$$

into mathematical symbols, refer to Figure 32.1. Equation (32.1) can be applied to the mass of a single species or to the total amount of material or energy in the system. Let us write each of the terms in Eq. (32.1) in mathematical symbols for a very small time interval Δt . Let the accumulation be positive in the direction in which time is positive, that is, as time increases from t to $t + \Delta t$. Then, using the component mass balance as an example, the accumulation will be the mass of A in the system at time $t + \Delta t$ minus the mass of A in the system at time t ,

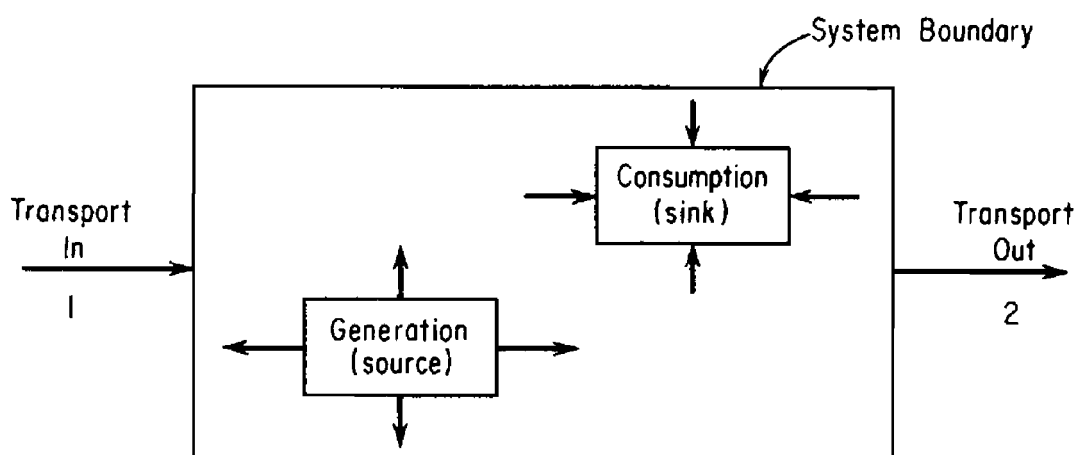


Figure 32.1 General unsteady-state process with transport in and out and internal generation and consumption.

$$\text{accumulation} = \rho_A V|_{t+\Delta t} - \rho_A V|_t$$

where ρ_A = mass of component A per unit volume
 V = volume of the system

and the symbol $|_t$ means that the quantities preceding the vertical line are evaluated at time t , or time $t + \Delta t$, or at surface S_1 , or at surface S_2 , as the case may be as denoted by the subscript. Note that the net dimensions of the accumulation term are the mass of A.

We shall split the mass transport across the system boundary into two parts, transport through defined surfaces S_1 and S_2 whose areas are known, and transport across the system boundary through other (undefined) surfaces. The net transport of A into (through S_1) and out of (through S_2) the system through defined surfaces can be written as:

$$\text{net flow across boundary via } S_1 \text{ and } S_2 = \rho_A v S \Delta t|_{S_1} - \rho_A v S \Delta t|_{S_2}$$

where v = fluid velocity in a duct of cross section S
 S_i = defined cross-sectional area perpendicular to material flow.

Again note that the net dimensions of the transport term are the mass of A. Other types of transport across the system boundary can be represented by

$$\text{net residual flow across boundary} = \dot{w}_A \Delta t$$

where \dot{w}_A is the rate of mass flow of component A through the system boundaries other than the defined surfaces S_1 and S_2 .

Finally, the net generation-consumption term will be assumed to be due to a chemical reaction r_A :

$$\text{net generation-consumption} = \dot{r}_A \Delta t$$

where \dot{r}_A is the net rate of generation-consumption of component A by chemical reaction.

Introduction of all these terms into Eq. (32.1) gives Eq. (32.2). Equations (32.3) and (32.4) can be developed from exactly the same type of analysis. Try to formulate Eqs. (32.3) and (32.4) yourself.

The species material balance for species A is:

$$\underbrace{\rho_A V|_{t+\Delta t} - \rho_A V|_t}_{\text{accumulation}} = \underbrace{\rho_A v S \Delta t|_{S_1}}_{\text{transport through defined boundaries}} - \underbrace{\rho_A v S \Delta t|_{S_2}}_{\text{transport through other boundaries}} + \underbrace{\dot{w}_A \Delta t + \dot{r}_A \Delta t}_{\text{generation or consumption}} \quad (32.2)$$

The total material balance is:

$$\underbrace{\rho V|_{t+\Delta t} - \rho V|_t}_{\text{accumulation}} = \underbrace{\rho v S \Delta t|_{S_1} - \rho v S \Delta t|_{S_2}}_{\text{transport through defined boundaries}} + \underbrace{\dot{w} \Delta t}_{\text{transport through other boundaries}} \quad (32.3)$$

By an analogous procedure we can formulate the energy balance:

$$\underbrace{E|_{t+\Delta t} - E|_t}_{\text{accumulation}} = \underbrace{\left| \left(\hat{H} + \frac{v^2}{2} + gh \right) \dot{m} \Delta t \right|_{S_1} - \left| \left(\hat{H} + \frac{v^2}{2} + gh \right) \dot{m} \Delta t \right|_{S_2}}_{\text{transport through defined boundaries}} + \underbrace{\dot{Q} \Delta t}_{\text{heat}} + \underbrace{\dot{W} \Delta t}_{\text{work}} + \underbrace{\dot{B} \Delta t}_{\text{transport through other boundaries}} \quad (32.4)$$

where \dot{B} = rate of energy transfer accompanying \dot{w}

\dot{m} = rate of mass transfer through defined surfaces S_1 in and S_2 out, respectively

\dot{Q} = rate of heat transfer to system

\dot{W} = rate of work done on the system

\dot{w} = rate of total mass flow through the system boundaries other than through the defined surfaces S_1 and S_2

The other notation for the material and energy balances is identical to that of Chapters 21 to 26; note that the work, heat, generation, and mass transport are now all expressed as rate terms (mass or energy per unit time).

If each side of Eq. (32.2) is divided by Δt we obtain

$$\frac{\rho_A V|_{t+\Delta t} - \rho_A V|_t}{\Delta t} = \rho_A v S|_{S_1} - \rho_A v S|_{S_2} + \dot{w}_A + \dot{r}_A \quad (32.5)$$

Similar relations can be obtained from Eqs. (32.3) and (32.4). If we take the limit of each side of Eq. (32.5) as $\Delta t \rightarrow 0$, we get a differential equation

$$\frac{d(\rho_A V)}{dt} = -\Delta(\rho_A v S) + \dot{w}_A + \dot{r}_A \quad (32.6)$$

and analogously the total mass balance and the energy balance, respectively, are

$$\frac{d(\rho V)}{dt} = -\Delta(\rho v S) + \dot{w} \quad (32.7)$$

$$\frac{d(E)}{dt} = \dot{Q} + \dot{W} + \dot{B} - \Delta \left[\left(\hat{H} + \frac{v^2}{2} + gh \right) \dot{m} \right] \quad (32.8)$$

Can you get Eqs. (32.7) and (32.8) from (32.3) and (32.4), respectively? Try it.

The relation between the energy balance given by Eq. (32.8), which has the units of energy per unit time, and the energy balance given by Eq. (22.6), which has the units of energy, should now be fairly clear. Equation (22.6) represents the integration of Eq. (32.8) with respect to time, expressed formally as follows:

$$E_{t_2} - E_{t_1} = \int_{t_1}^{t_2} \{ \dot{Q} + \dot{B} + \dot{W} - \Delta[(\hat{H} + \hat{K} + \hat{P})\dot{m}] \} dt \quad (32.9)$$

The quantities designated in Eqs. (22.6) without the superscript dot are the respective integrated values from Eq. (32.9).

To solve one or any combination of the very general equations (32.6), (32.7), or (32.8) analytically may be quite difficult, and in the following examples we shall have to restrict our analyses to simple cases. If we make enough (reasonable) assumptions and work with simple problems, we can consolidate or eliminate enough terms of the equations to be able to integrate them and develop some analytical answers. If analytical solutions are not possible, then a computer code can be used to get a numerical solution for a specific case.

In the formulation of unsteady-state equations you apply the usual procedures of problem solving discussed in previous chapters. You can set up the equation as in Eqs. (32.2)–(32.4) or use the differential equations (32.6)–(32.8) directly. To complete the problem formulation you must include some known value of the dependent variable (or its derivative) at a specified time, usually the **initial condition**.

We are now going to examine some very simple unsteady-state problems. You can (and will) find more complicated examples in texts dealing with all phases of mass transfer, heat transfer, and fluid dynamics.

EXAMPLE 32.1 Unsteady-State Material Balance without Generation

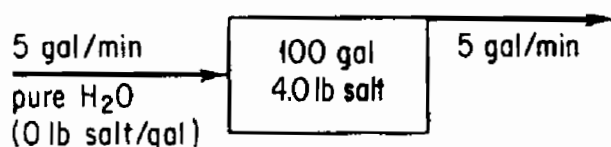
A tank holds 100 gal of a water-salt solution in which 4.0 lb of salt is dissolved. Water runs into the tank at the rate of 5 gal/min and salt solution overflows at the same rate. If the mixing in the tank is adequate to keep the concentration of salt in the tank uniform at all times, how much salt is in the tank at the end of 50 min? Assume that the density of the salt solution is essentially the same as that of water.

Solution

We shall set up from scratch the differential equations that describe the process. The basis will be 50 min.

Step 2

Draw a picture, and put down the known data. See Figure E32.1.

**Figure E32.1****Step 3**

Choose the independent and dependent variables. Time, of course, is the independent variable, and either the salt quantity or concentration of salt in the tank can be the dependent variable. Suppose that we make the mass (quantity) of salt the dependent variable. Let $x = \text{lb of salt in the tank at time } t$.

Step 4

Write the known value of x at a given value of t . This is the initial condition:

$$\text{at } t = 0 \quad x = 4.0 \text{ lb}$$

Steps 6, 7, and 8

It is easy to make a total material balance and a component material balance on the salt. (No energy is needed because the system can be assumed to be isothermal.)

Total balance:

$$\begin{array}{c}
 \text{accumulation} \qquad \qquad \qquad \text{in} \\
 [m_{\text{tot}} \text{ lb}]_{t+\Delta t} - [m_{\text{tot}} \text{ lb}]_t = \frac{5 \text{ gal}}{\text{min}} \left| \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right| \left| \frac{\rho_{\text{H}_2\text{O}} \text{ lb}}{\text{ft}^3} \right| \frac{\Delta t \text{ min}}{1} \\
 \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{out} \\
 - \frac{5 \text{ gal}}{\text{min}} \left| \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right| \left| \frac{\rho_{\text{soln}} \text{ lb}}{\text{ft}^3} \right| \frac{\Delta t \text{ min}}{1}
 \end{array}$$

This equation tells us that the flow of water into the tank equals the flow of solution out of the tank if $\rho_{\text{H}_2\text{O}} = \rho_{\text{soln}}$ as assumed.

Salt balance:

$$\begin{array}{c}
 \text{accumulation} \qquad \text{in} \qquad \qquad \text{out} \\
 [x \text{ lb}]_{t+\Delta t} - [x \text{ lb}]_t = 0 - \frac{5 \text{ gal}}{\text{min}} \left| \frac{x \text{ lb}}{100 \text{ gal}} \right| \frac{\Delta t \text{ min}}{1}
 \end{array}$$

Dividing by Δt and taking the limit as Δt approaches zero,

$$\lim_{\Delta t \rightarrow 0} \frac{[x]_{t+\Delta t} - [x]_t}{\Delta t} = -0.05x$$

or

$$\frac{dx}{dt} = -0.05x \quad (a)$$

Notice how we have kept track of the units in the normal fashion in setting up these equations. Because of our assumption of uniform concentration of salt in the tank, the concentration of salt leaving the tank is the same as that in the tank, or x lb/100 gal of solution.

Step 9

Solve the unsteady-state material balance on the salt. By separating the independent and dependent variables we get

$$\frac{dx}{x} = -0.05 dt$$

This equation can be integrated between the definite limits of

$$t = 0 \quad x = 4.0$$

$$t = 50 \quad X = \text{the unknown value of } x \text{ lb}$$

$$\int_{4.0}^X \frac{dx}{x} = -0.05 \int_0^{50} dt$$

$$\ln \frac{X}{4.0} = -2.5 \quad X = \frac{4.0}{12.2} = 0.328 \text{ lb salt}$$

An equivalent differential equation to Eq. (a) can be obtained directly from the component mass balance in the form of Eq. (32.6) if we let ρ_A = concentration of salt in the tank at any time t in terms of lb/gal:

$$\frac{d(\rho_A V)}{dt} = - \left(\frac{5 \text{ gal}}{\text{min}} \left| \frac{\rho_A \text{ lb}}{\text{gal}} \right| \right) - 0$$

If the tank holds 100 gal of solution at all times, V is a constant and equal to 100, so that

$$\frac{d\rho_A}{dt} = -\frac{5\rho_A}{100} \quad (b)$$

The initial conditions are

$$\text{at } t = 0 \quad \rho_A = 0.04$$

The solution of Eq. (b) would be carried out exactly as the solution of Eq. (a).

EXAMPLE 32.2 Unsteady-State Material Balance without Generation

A square tank 4 m on a side and 10 m high is filled to the brim with water. Find the time required for it to empty through a hole in the bottom 5 cm² in area.

Solution**Step 2**

Draw a diagram of the process, and put down the data. See Figure E32.2a.

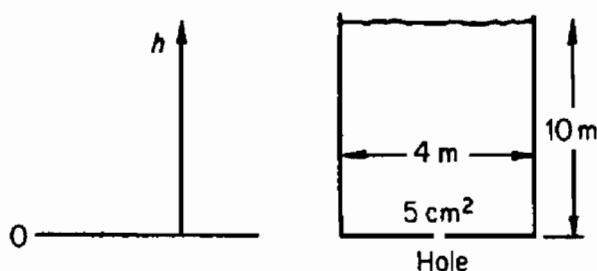


Figure E32.2a

Step 3

Select the independent and dependent variables. Again, time will be the independent variable. We could select the quantity of water in the tank as the dependent variable, but since the cross section of the tank is constant, let us choose h , the height of the water in the tank, as the dependent variable.

Step 4

Write the known value of h at the given time t :

$$\text{at } t = 0 \quad h = 10 \text{ m}$$

Steps 5, 6, 7, and 8

Develop the unsteady-state balance(s) for the process. In an elemental of time Δt , the height of the water in the tank drops Δh . The mass of water leaving the tank is in the form of a cylinder 5 cm² in area, and we can calculate the quantity as

$$\frac{5 \text{ cm}^2}{1} \left| \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^2 \right| \left| \frac{v^* \text{ m}}{\text{s}} \right| \left| \frac{\rho \text{ kg}}{\text{m}^3} \right| \left| \frac{\Delta t \text{ s}}{1} \right| = 5 \times 10^{-4} v^* \rho \Delta t \text{ kg}$$

where ρ = density of water

v^* = average velocity of the water leaving the tank

The depletion of water inside the tank in terms of the variable h , expressed in kg, is

$$\frac{16 \text{ m}^2}{1} \left| \frac{\rho \text{ kg}}{\text{m}^3} \right| \left| \frac{h \text{ m}}{1} \right| \Big|_{t+\Delta t} - \frac{16 \text{ m}^2}{1} \left| \frac{\rho \text{ kg}}{\text{m}^3} \right| \left| \frac{h \text{ m}}{1} \right| \Big|_t = 16 \rho \Delta h \text{ kg}$$

An overall material balance is

$$\begin{array}{ccc} \text{accumulation} & \text{in} & \text{out} \\ 16\rho\Delta h = 0 - 5 \times 10^{-4} \rho v^* \Delta t \end{array} \quad (\text{a})$$

Note that Δh will have a negative value, but our equation takes account of this automatically; the accumulation is really a depletion. You can see that the term ρ , the density of water, cancels out, and we could just have well made our material balance on a volume of water.

Equation (a) becomes

$$\frac{\Delta h}{\Delta t} = -\frac{5 \times 10^{-4} v^*}{16}$$

Taking the limit as Δh and Δt approach zero, we get the differential equation

$$\frac{dh}{dt} = -\frac{5 \times 10^{-4} v^*}{16} \quad (\text{b})$$

Steps 8 and 9

Unfortunately, this is an equation with one independent variable, t , and two dependent variables, h and v^* . We must find another equation to eliminate either h or v^* if we want to obtain a solution. Since we want our final equation to be expressed in terms of h , the next step is to find some function to relate v^* to h and t , and then we can substitute for v^* in the unsteady-state equation, Eq. (b).

We shall employ the steady-state mechanical energy balance equation for an incompressible fluid, discussed in Chapter 27, to relate v^* and h . See Figure E32.2b. With $W = 0$ and $E_v = 0$ the steady state mechanical energy balances reduce to

$$\Delta \left(\frac{(v^*)^2}{2} + gh \right) = 0 \quad (\text{c})$$

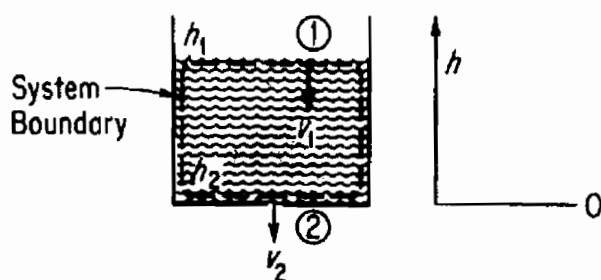


Figure E32.2b

We have assumed that the atmosphere pressure is the same at section 1—the water surface—and section 2—the hole—for the system consisting of the water in the tank. Equation (c) can be rearranged to

$$\frac{(v_2^*)^2 - (v_1^*)^2}{2} + g(h_2 - h_1) = 0 \quad (\text{d})$$

where v_2^* = exit velocity through the 5 cm² hole at boundary 2
 v_1^* = velocity of water in the tank at boundary 1

If $v_1^* \cong 0$, a reasonable assumption for the water in the large tank at any time, at least compared to v_2^* , we have

$$\begin{aligned}(v_2^*)^2 &= -2g(0 - h_1) = 2gh \\ v_2^* &= \sqrt{2gh}\end{aligned}\tag{e}$$

Because the exit-stream flow is not frictionless and because of turbulence and orifice effects in the exit hole, we must correct the value of v given by Eq. (e) for frictionless flow by an empirical adjustment factor as follows:

$$v_2^* = c\sqrt{2gh}\tag{f}$$

where c is an orifice correction that we could find (from a text discussing fluid dynamics) with a value of 0.62 for this case. Thus

$$v_2^* = 0.62\sqrt{2(9.80)h} = 2.74\sqrt{h} \text{ m/s}$$

Let us substitute this relation into Eq. (b) in place of v^* . Then we obtain

$$\frac{dh}{dt} = \frac{(5.0 \times 10^{-4})(2.74)(h)^{1/2}}{16}\tag{g}$$

Equation (g) can be integrated between

$$h = 10 \text{ m at } t = 0$$

and

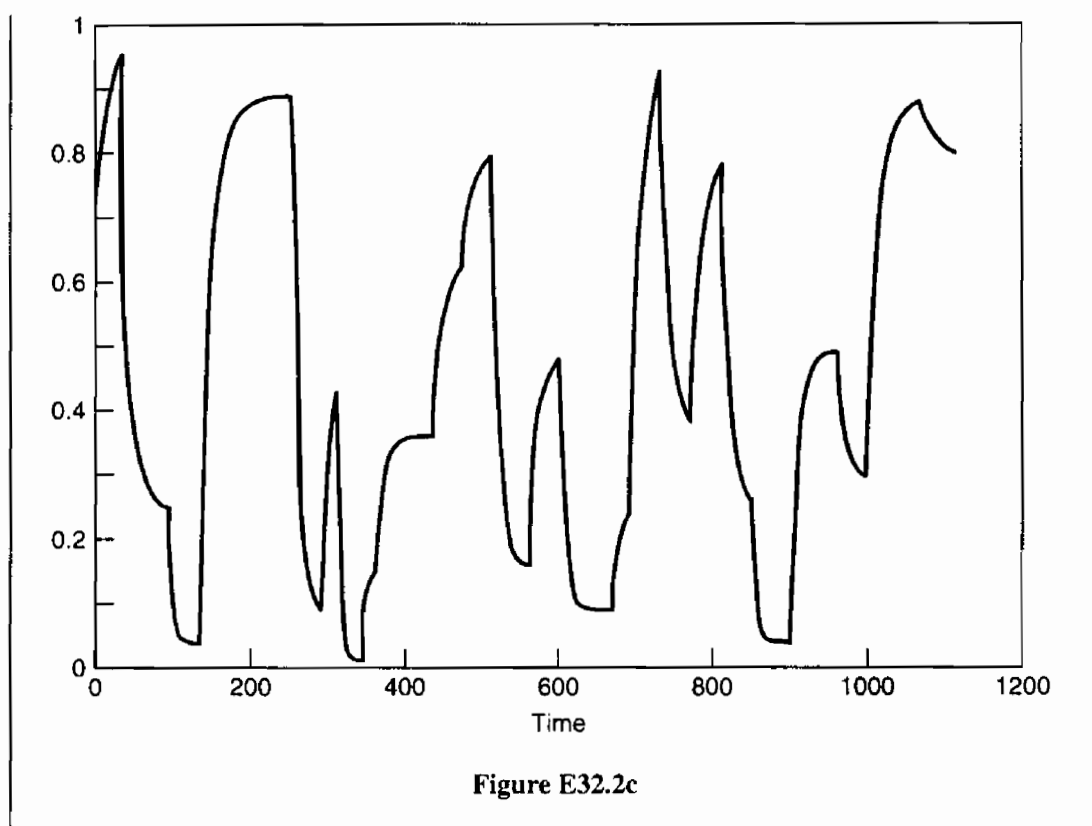
$$h = 0 \text{ m at } t = \theta, \text{ the unknown time}$$

$$-1.17 \times 10^4 \int_{10}^0 \frac{dh}{h^{1/2}} = \int_0^\theta dt$$

to yield

$$\theta = 1.17 \times 10^4 \int_0^{10} \frac{dh}{h^{1/2}} = 1.17 \times 10^4 [2\sqrt{h}]_0^{10} = 7.38 \times 10^4 \text{ s}$$

Now suppose that in addition to the loss of fluid through the hole in the bottom of the tank additional fluid is poured continuously into the top of the tank at varying rates. Numerical integration of the resulting differential equations yields a varying height of fluid as illustrated in Figure E32.2c.



EXAMPLE 32.3 Material Balance in Batch Distillation

A small still is separating propane and butane at 135°C, and initially contains 10 kg moles of a mixture whose composition is $x = 0.30$ (x = mole fraction butane). Additional mixture ($x_F = 0.30$) is fed at the rate of 5 kg mol/hr. If the total volume of the liquid in the still is constant, and the concentration of the vapor from the still (x_D) is related to x_S as follows:

$$x_D = \frac{x_S}{1 + x_S} \quad (\text{a})$$

how long will it take for the value of x_S to change from 0.3 to 0.4? What is the steady-state ("equilibrium") value of x_S in the still (i.e., when x_S becomes constant?) See Figure E32.3.

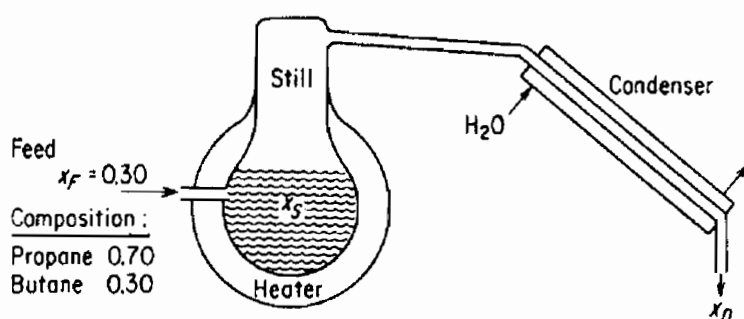


Figure E32.3

Solution

Since butane and propane form ideal solutions, we do not have to worry about volume changes on mixing or separation. Only the material balance is needed to answer the questions posed. If t is the independent variable and x_S is the dependent variable, we can say that

Butane Balance (C_4): The input to the still is:

$$\frac{5 \text{ mol feed}}{\text{hr}} \left| \frac{0.30 \text{ mol } C_4}{\text{mol feed}} \right.$$

The output from the still is equal to the amount condensed

$$\frac{5 \text{ mol cond.}}{\text{hr}} \left| \frac{x_D \text{ mol } C_4}{\text{mol condensed}} \right.$$

The accumulation is $\frac{10 dx_S}{dt}$

Our unsteady state equation is then

accumulation in out

$$\frac{dx_S}{dt} = 0.15 - 0.5x_D \quad (b)$$

As in Example 32.2, it is necessary to reduce the equation to one dependent variable by substituting for x_D from Eq. (a) in Eq. (b)

$$\frac{dx_S}{dt} = 0.15 - \frac{x_S}{1 + x_S}(0.5) \quad (c)$$

Integration of Eq. (c) between the following limits

$$\begin{array}{ll} \text{at } t = 0 & x_S = 0.30 \\ t = \theta & x_S = 0.40 \end{array}$$

$$\int_{0.30}^{0.40} \frac{dx_S}{0.15 - [0.5x_S/(1 + x_S)]} = \int_0^\theta dt = \theta$$

$$\int_{0.30}^{0.40} \frac{(1 + x_S) dx_S}{0.15 - 0.35x_S} = \theta = \left[-\frac{x_S}{0.35} - \frac{1}{(0.35)^2} \ln(0.15 - 0.35x_S) \right]_{0.30}^{0.40}$$

gives $\theta = 5.85$ hr

If you only had experimental data for x_D as a function of x_S instead of the given equation, you could always integrate the equation numerically.

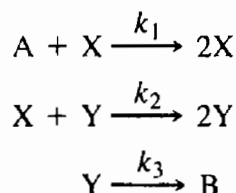
The steady-state value of x_S is established at infinite time or, alternatively, when the accumulation is zero. At that time,

$$0.15 = \frac{0.5x_S}{1 + x_S} \quad \text{or} \quad x_S = 0.428$$

The value of x_S could never be any greater than 0.428 for the given conditions.

EXAMPLE 32.4 Oscillating Reactions

In an isothermal reactor the following reactions take place



where A is the initial reactant, X and Y are intermediate species, and B is the final product of the reaction. A is maintained at a constant value by starting with so much A that only X, Y, and B vary with time.

Develop the unsteady state material balance equations that predict the change of X and Y as a function of time for the initial conditions $c_X(0) = 30$ and $c_Y(0) = 90$ (c designates concentration).

Solution

The macroscopic balance for both species X and Y, is

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} - \text{consumption}$$

For a batch (closed) system, the reactor, the in and out terms are zero. The generation and consumption terms are formulated by using concepts from chemical kinetics

	<u>X</u>	<u>Y</u>
generation:	$k_1 c_A c_X$	$k_2 c_X c_Y$
consumption:	$k_2 c_X c_Y$	$k_3 c_Y$

and the derivatives represent the accumulation. We can merge $k_1 c_A$ into a constant k_1^* since c_A is constant. Then the differential equations for X and Y are

$$\frac{dc_X}{dt} = k_1^* c_X - k_2 c_X c_Y \quad (a)$$

$$\frac{dc_Y}{dt} = k_2 c_X c_Y - k_3 c_Y \quad (b)$$

Figure E32.4a shows the concentrations of X and Y for the values $k_1^* = 70$, $k_2 = 1$, and $k_3 = 70$ when (a) and (b) are solved using a computer code.

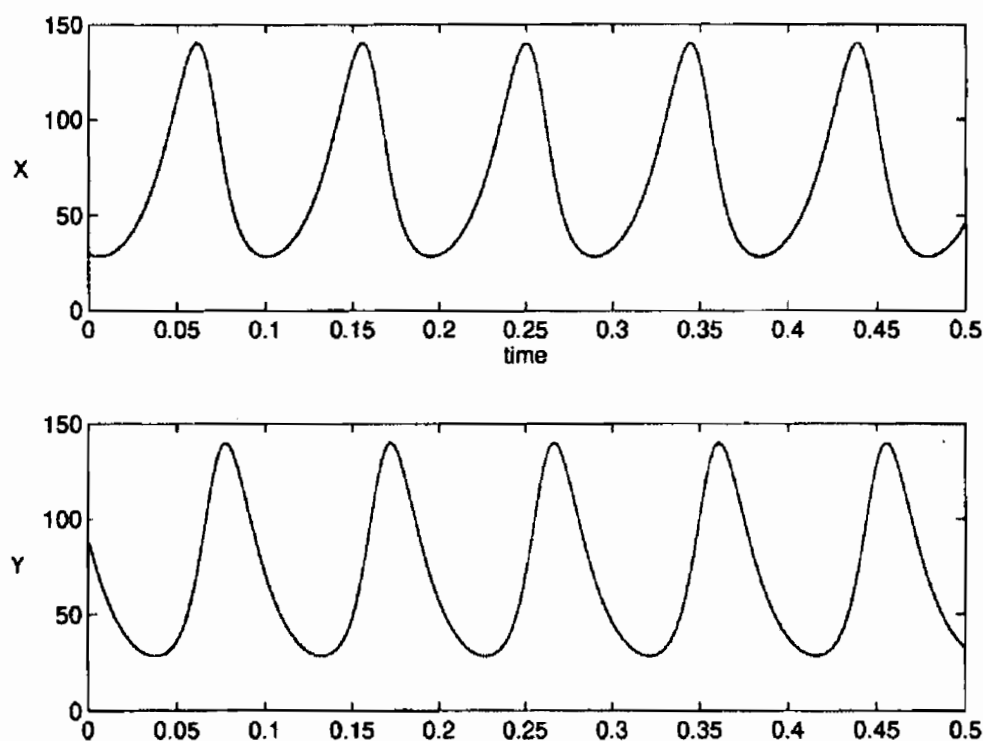


Figure E32.4a

In the steady state, the intermediates exhibit an interesting phenomena. Divide Eq. (b) by Eq. (a) to get

$$\frac{dc_Y}{dc_X} = \frac{c_Y[k_2 c_X - k_3]}{c_X[k_1^* - k_2 c_Y]}$$

which can be arranged to

$$\frac{(k_1^* - k_2 c_Y)}{c_Y} dc_Y = \frac{(k_2 c_X - k_3)}{c_X} dc_X \quad (c)$$

Integration of Eq. (c) yields

$$k_1^* \ln c_Y - k_2 c_Y + k_3 \ln c_X - k_2 c_X = \text{constant} \quad (d)$$

Eq. (d) represents a series of closed loops when c_Y is plotted against c_X ; the constant can be evaluated from the initial conditions for c_X and c_Y . Examine Figure E32.4b.

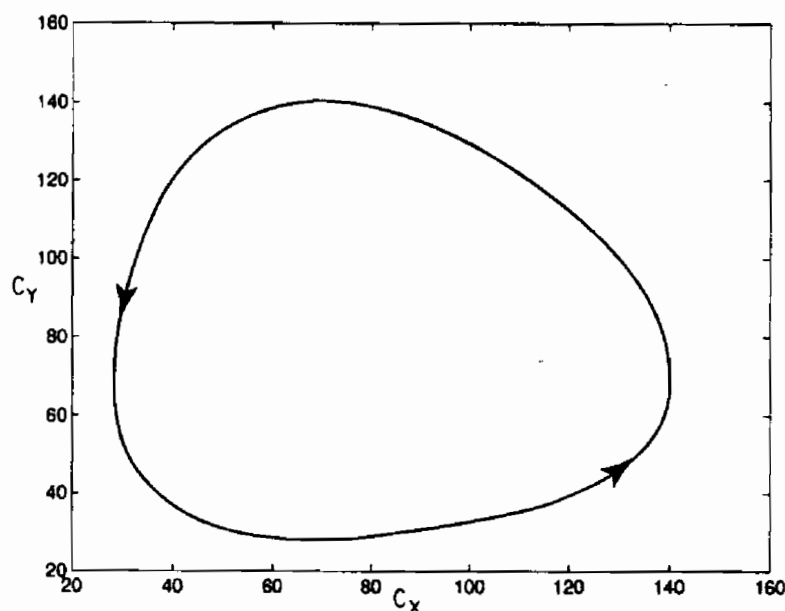


Figure E32.4b

EXAMPLE 32.5 Unsteady-State Energy Balance

Oil initially at 60°F is being heated in a stirred (perfectly mixed) tank by saturated steam which is condensing in the steam coils at 40 psia. If the rate of heat transfer is given by Newton's heating law,

$$\dot{Q} = \frac{dQ}{dt} = h(T_{\text{steam}} - T_{\text{oil}})$$

where Q is the heat transferred in Btu and h is the heat transfer coefficient in the proper units, how long does it take for the discharge from the tank to rise from 60°F to 90°F? What is the maximum temperature that can be achieved in the tank?

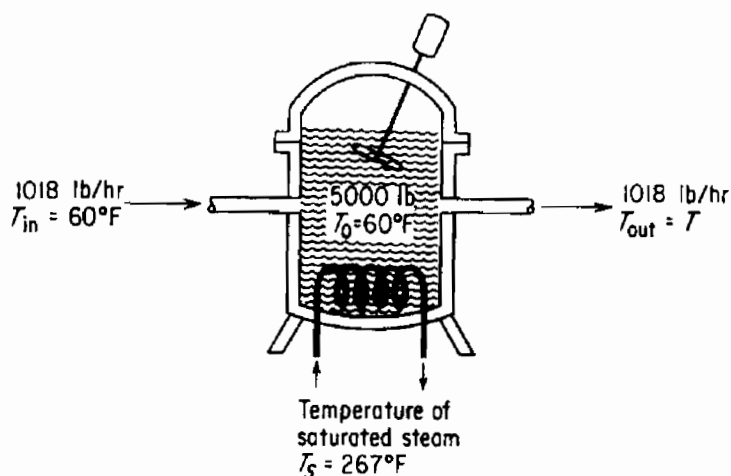


Figure E32.5

Additional Data:

Motor horsepower	=	1 hp; efficiency is 0.75
Initial amount of oil in tank	=	5000 lb
Entering oil flow rate	=	1018 lb/hr at a temperature of 60°F
Discharge oil flow rate	=	1018 lb/hr at a temperature of T
h	=	291 Btu/(hr)(°F)
C_{poil}	=	0.5 Btu/(lb)(°F)

Solution

The process is shown in Figure E32.5. The system is the oil in the tank. The independent variable will be t , the time; the dependent variable will be the temperature of the oil in the tank, which is the same as the temperature of the oil discharged. The material balance is not needed because the process, insofar as the quantity of oil is concerned, is assumed to be in the steady-state.

The first step is to set up the unsteady-state energy balance. Let T_s = the steam temperature and T = the oil temperature. The balance per unit time is

$$\text{accumulation} = \text{input} - \text{output}$$

$$\frac{dE}{dt} = \frac{dU}{dt} = Q - \Delta H$$

The rate of change of energy inside the tank is nothing more than the rate of change of internal energy, which, in turn, is essentially the same as the rate of change of enthalpy (i.e., $dE/dt = dU/dt = dH/dt$) because $d(pV)/dt \approx 0$.

A good choice for a reference temperature for the enthalpies is 60°F because the choice makes the input enthalpy zero.

$$\begin{array}{l}
 \left. \begin{array}{l}
 \text{rate of enthalpy of} \\
 \text{the input stream}
 \end{array} \right\} \frac{1018 \text{ lb}}{\text{hr}} \left| \frac{0.5 \text{ Btu}}{(\text{lb})(^\circ\text{F})} \right| \frac{60^\circ\text{F} - 60^\circ\text{F}}{T_{\text{in}} - T_{\text{ref}}} = 0 \\
 \left. \begin{array}{l}
 \text{rate of} \\
 \text{heat transfer}
 \end{array} \right\} h(T_s - T) = \frac{291 \text{ Btu}}{(\text{hr})(^\circ\text{F})} \left| \frac{(267 - T)^\circ\text{F}}{1} \right|
 \end{array} \right\} \text{input (Btu)}$$

$$\begin{array}{l}
 \text{rate of enthalpy of} \\
 \text{the output stream}
 \end{array} \frac{1018 \text{ lb}}{\text{hr}} \left| \frac{0.5 \text{ Btu}}{(\text{lb})(^\circ\text{F})} \right| \frac{(T - 60)^\circ\text{F}}{1} \quad \text{output (Btu)}$$

$$\begin{array}{l}
 \text{rate of enthalpy change} \\
 \text{inside the tank}
 \end{array} \frac{5000 \text{ lb}}{1} \left| \frac{0.5 \text{ Btu}}{(\text{lb})(^\circ\text{F})} \right| \frac{dT(^\circ\text{F})}{dt(\text{hr})} \quad \text{accumulation (Btu)}$$

The energy introduced by the motor enters the tank as rate of work, \dot{W} .

$$\text{rate of work} \quad \dot{W} = \frac{3 \text{ hp}}{4} \left| \frac{0.7608 \text{ Btu}}{(\text{sec})(\text{hp})} \right| \frac{3600 \text{ sec}}{1 \text{ hr}} = \frac{1910 \text{ Btu}}{\text{hr}}$$

Then

$$2500 = 291(267 - T) - 509(T - 60) + 1910$$

$$\frac{dT}{dt} = 44.1 - 0.32T$$

$$\int_{60}^{90} \frac{dT}{44.1 - 0.32T} = \int_0^{\theta} dt = \theta$$

$$\theta = 1.52 \text{ hr.}$$

EXAMPLE 32.6 Modeling a Calcination Process

The process flowsheet illustrated in Figure E32.6a is a fluidized bed in which granular solids are calcinated. Water vapor and gaseous decomposition products leave the bed with the fluidizing gas while metallic oxide products deposit on the particles in the fluidized bed. In Figure E32.6a, x is the mass concentration of the component of interest; F is the mass flow rate of the feed; x_0 is the concentration of x in F ; Q is the mass flow rate of stream 1 or 2, respectively; P is the mass flow rate of product; and V is the mass of inventory at time t in vessel 1 or 2, respectively. The overlay dots (\cdot) have been suppressed.

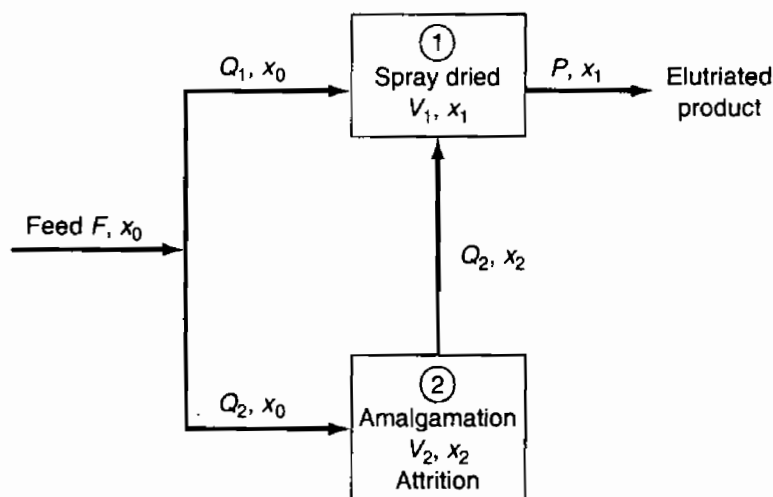


Figure E32.6a

The mass balances for each vessel after introduction of x_0 into stream F become: accumulation = in - out if we ignore any reactions

Vessel 1

$$\text{Total mass} \quad \frac{dV_1}{dt} = Q_1 + Q_2 - P = 0 \quad (\text{a})$$

$$\text{Component mass} \quad V_1 \frac{dx_1}{dt} = Q_1 x_0 + Q_2 x_2 - P x_1 \quad (\text{b})$$

$$\text{Initial condition} \quad x_1(0) = 0$$

Vessel 2

$$\text{Total mass} \quad \frac{dV_2}{dt} = Q_2 - Q_2 = 0 \quad (c)$$

$$\text{Component mass} \quad V_2 \frac{dx_2}{dt} = Q_2 x_0 - Q_2 x_2 \quad (d)$$

$$\text{Initial condition} \quad x_2(0) = 0$$

After x_0 is removed from stream F , the concentration of x_0 becomes 0 in the model.

Figure E32.6b shows the value of x_1 as a function of time t for the values $P = 16.5$ g/min, $Q_2 = 6.5$ g/min, $V_1 = 600$ g, and $V_2 = 2.165 \times 10^4$ g when the component of interest is added and then removed from the feed F , and the stated values of the parameters were obtained from experiments.

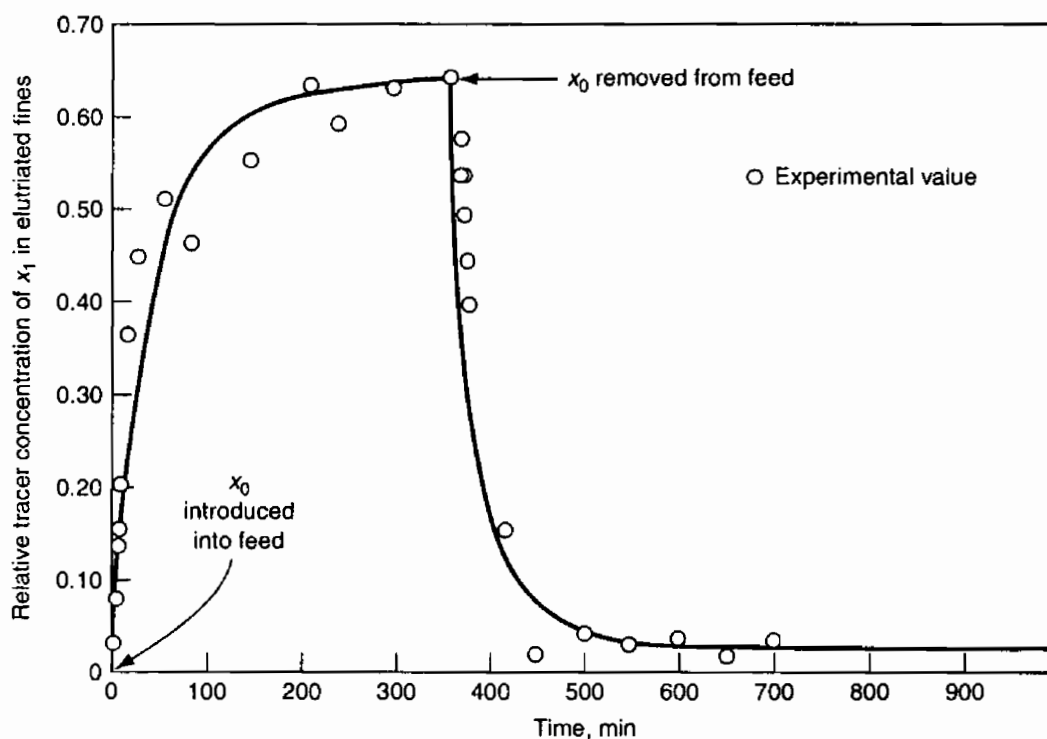


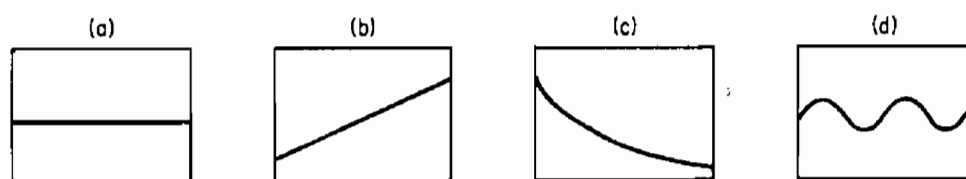
Figure E32.6b

Looking Back

In the section we explained how to formulate unsteady-state material and energy balances in which the variation with time is of interest.

SELF-ASSESSMENT TEST**Questions**

1. In a batch type of chemical reactor, do you have to have the starting conditions to predict the yield?
2. Is time the independent or dependent variable in macroscopic unsteady-state equations?
3. How can you obtain the steady-state balances from Eqs. (32.6)–(32.8)?
4. Which of the following plots in Figure SA32.Q1–4 of response vs. time are not transient-state processes?

**Figure SA32.Q1–4**

5. Group the following words in sets of synonyms: (1) response, (2) input variable, (3) parameter, (4) state variable, (5) system parameter, (6) initial condition, (7) output, (8) independent variable, (9) dependent variable, (10) coefficient, (11) output variable, (12) constant.

Problems

1. A chemical inhibitor must be added to the water in a boiler to avoid corrosion and scale. The inhibitor concentration must be maintained between 4 and 30 ppm. The boiler system always contains 100,000 kg of water and the blowdown (purge) rate is 15,000 kg/hr. The makeup water contains no inhibitor. An initial 2.8 kg of inhibitor is added to the water and thereafter 2.1 kg is added periodically. What is the maximum time interval (after the 2.8 kg) until the first addition of the inhibitor should take place?
2. In a reactor a small amount of undesirable byproduct is continuously formed at the rate of 0.5 lb/hr when the reactor contains a steady inventory of 10,000 lb of material. The reactor inlet stream contains traces of the byproduct (40 ppm), and the effluent stream is 1400 lb/hr. If on startup, the reactor contains 5000 ppm of the byproduct, what will be the concentration in ppm at 10 hr?

Thought Problems

1. Refer to the tank in Example 32.2. If the square tank is replaced by (a) a vertical cylindrical tank, (b) a conical tank with vertex at the bottom, (c) a horizontal cylindrical tank, or (d) a spherical tank with the parameters shown in Figure TP32.1P1, if h and D are the same in each tank at $t = 0$, which tank will be the first to drain completely?

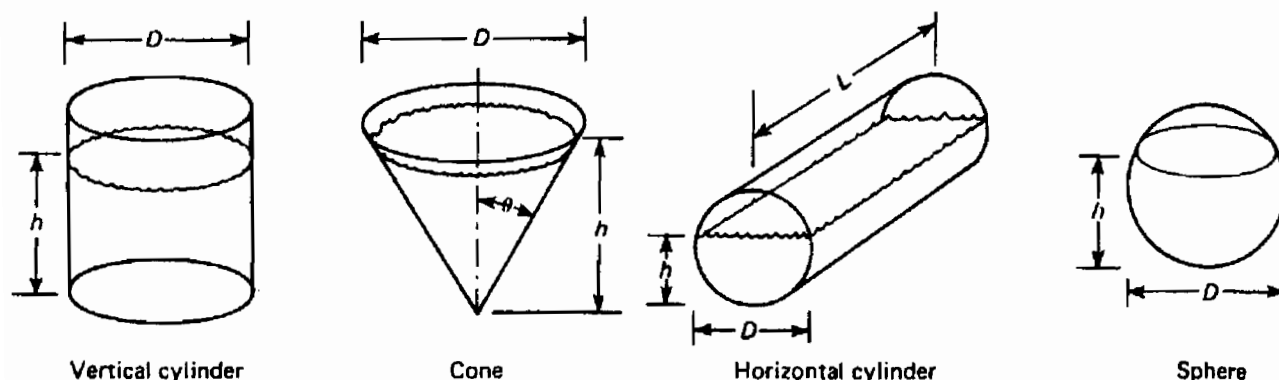


Figure TP32.1P1

2. Many chemical plant operations require that vessels and piping be inerted or purged. If a vessel is to be opened for maintenance or repair, for example, and if the vessel has contained either toxic or flammable materials, purging is required before workers can enter the vessel. For vessel entry, piping leading to or from the vessel will have to be blanked off and at least the portions of the vessels that are open to the pipe will have to be purged as well. Purging must be continued until the atmosphere in the vessel is safe for entry.

If the chemical in the vessel is flammable, purging must be accomplished in two steps: first, the flammable material is purged from the vessel with an inert gas such as nitrogen, and the nitrogen is then purged with air. When a vessel that is to be used for storing or processing flammable chemicals is initially put into service, it must be purged with an inert gas before flammable chemical are put in the vessel. This step is required to assure that a flammable mixture of the chemical and the air in the tank does not form.

Regardless of the method used to purge the equipment, the final step should be to check the atmosphere in the equipment to make certain that the concentration of the flammable or toxic material has been reduced to safe levels. For tank entry, the oxygen concentration must also be checked before the tank is entered. The measurement of residual concentrations is sometimes required by law; it is always needed for good practice.

Suppose that a 150-ft^3 tank containing air is to be inerted to a 1% oxygen concentration. Pure nitrogen is available for the job. The tank has a maximum allowable working pressure of 150 psia, so either of two methods is possible. In the first method, air is purged by a continuous sweep of nitrogen. The nitrogen is simply allowed to flow into the tank at essentially atmospheric pressure. It is assumed that the nitrogen mixes rapidly and completely with the air in the tank, so the gas leaving the tank has the same concentration of oxygen as the gas in the tank.

In the second technique, the tank is pressurized, the pure nitrogen inlet stream is turned off, and the gas mixture in the tank is then exhausted, lowering the pressure in the tank to atmospheric pressure. If the pressurization technique is used, multiple pressurization cycles may be required, with the tank returned to atmospheric pressure at the end of each cycle. Complete mixing is assumed for each cycle.

In this problem, you may assume that both nitrogen and air behave as ideal gases and that the temperature remains constant at 80°F throughout the process. Determine the volume of nitrogen (measured at standard conditions of 1.0 atm and 0°C) required to

purge the tank using each purging technique. For the pressurization technique, assume the pressure in the tank is raised to 140 psig (a little below its maximum working pressure) with nitrogen and then vented to 0 psig. This problem was adapted from the publication *Safety, Health, and Loss Prevention in Chemical Processes*, American Institute of Chemical Engineers, New York, 1990.

SUPPLEMENTARY REFERENCES

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Web Sites

www.hyprotech.com
www.aspentech.com
www.intergraph.com

PROBLEMS

- 32.1** A tank containing 100 kg of a 60% brine (60% salt) is filled with a 10% salt solution at the rate of 10 kg/min. Solution is removed from the tank at the rate of 15 kg/min. Assuming complete mixing, find the kilograms of salt in the tank after 10 min.
- 32.2** A defective tank of 1500 ft³ volume containing 100% propane gas (at 1 atm) is to be flushed with air (at 1 atm) until the propane concentration reduced to less than 1%. At that concentration of propane the defect can be repaired by welding. If the flow rate of air into the tank is 30 ft³/min, for how many minutes must the tank be flushed out? Assume that the flushing operation is conducted so that the gas in the tank is well mixed.

- 32.3** A 2% uranium oxide slurry (2 lb UO_2 /100 lb H_2O) flows into a 100-gal tank at the rate of 2 gal/min. The tank initially contains 500 lb of H_2O and no UO_2 . The slurry is well mixed and flows out at the same rate at which it enters. Find the concentration of slurry in the tank at the end of 1 hr.
- 32.4** The catalyst in a fluidized-bed reactor of 200-m^3 volume is to be regenerated by contact with a hydrogen stream. Before the hydrogen can be introduced in the reactor, the O_2 content of the air in the reactor must be reduced to 0.1%. If pure N_2 can be fed into the reactor at the rate of $20\text{ m}^3/\text{min}$, for how long should the reactor be purged with N_2 ? Assume that the catalyst solids occupy 6% of the reactor volume and that the gases are well mixed.
- 32.5** An advertising firm wants to get a special inflated sign out of a warehouse. The sign is 20 ft in diameter and is filled with H_2 at 15 psig. Unfortunately, the door frame to the warehouse permits only 19 ft to pass. The maximum rate of H_2 that can be safely vented from the balloon is $5\text{ ft}^3/\text{min}$ (measured at room conditions). How long will it take to get the sign small enough to just pass through the door?
- (a) First assume that the pressure inside the balloon is constant so that the flow rate is constant.
- (b) Then assume the amount of amount of H_2 escaping is proportional to the volume of the balloon, and initially is $5\text{ ft}^3/\text{min}$.
- (c) Could a solution to this problem be obtained if the amount of escaping H_2 were proportional to the pressure difference inside and outside the balloon?
- 32.6** A plant at Canso, Nova Scotia, makes fish-protein concentrate (FPC). It takes 6.6 kg of whole fish to make 1 kg of FPC, and therein is the problem—to make money, the plant must operate most of the year. One of the operating problems is the drying of the FOC. It dries in the fluidized dryer at a rate approximately proportional to its moisture content. If a given batch of FPC loses one-half of its initial moisture in the first 15 min, how long will it take to remove 90% of the water in the batch of FPC?
- 32.7** Water flows from a conical tank at the rate of $0.020(2 + h^2)\text{ m}^3/\text{min}$, as shown in Figure P32.7. If the tank is initially full, how long will it take for 75% of the water to flow out of the tank? What is the flow rate at that time?

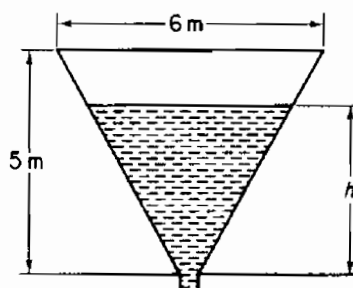
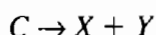


Figure P32.7

- 32.8** A sewage disposal plant has a big concrete holding tank of 100,000 gal capacity. It is three-fourths full of liquid to start with and contains 60,000 lb of organic material in

suspension. Water runs into the holding tank at the rate of 20,000 gal/hr and the solution leaves at the rate of 15,000 gal/hr. How much organic material is in the tank at the end of 3 hr?

- 32.9** Suppose that in problem 32.8 the bottom of the tank is covered with sludge (precipitated organic material) and that the stirring of the tank causes the sludge to go into suspension at a rate proportional to the difference between the concentration of sludge in the tank at any time and 10 lb of sludge/gal. If no organic material were present, the sludge would go into suspension at the rate of 0.05 lb/(min) (gal solution) when 75,000 gal of solution are in the tank. How much organic material is in the tank at the end of 3 hr?
- 32.10** In a chemical reaction the products X and Y are formed according to the equation



The rate at which each of these products is being formed is proportional to the amount of C present. Initially: $C = 1$, $X = 0$, $Y = 0$. Find the time for the amount of X to equal the amount of C .

- 32.11** A tank is filled with water. At a given instant two orifices in the side of the tank are opened to discharge the water. The water at the start is 3 m deep and one orifice is 2 m below the top while the other one is 2.5 m below the top. The coefficient of discharge of each orifice is known to be 0.61. The tank is a vertical right circular cylinder 2 m in diameter. The upper and lower orifices are 5 and 10 cm in diameter, respectively. How long will be required for the tank to be drained so that the water level is at a depth of 1.5 m?
- 32.12** Suppose that you have two tanks in series, as diagrammed in Figure P32.12. The volume of liquid in each tank remains constant because of the design of the overflow lines. Assume that each tank is filled with a solution containing 10 lb of A , and that the tanks each contain 100 gal of aqueous solution of A . If fresh water enters at the rate of 10 gal/hr, what is the concentration of A in each tank at the end of 3 hr? Assume complete mixing in each tank and ignore any change of volume with concentration.

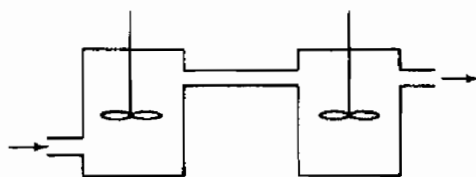


Figure P32.12

- 32.13.** A well-mixed tank has a maximum capacity of 100 gal and it is initially half full. The discharge pipe at the bottom is very long and thus it offers resistance to the flow of water through it. The force that causes the water to flow is the height of the water in the tank, and in fact that flow is just proportional to the height. Since the height is

proportional to the total volume of water in the tank, the volumetric flow rate of water out, q_o , is

$$q_o = kV$$

The flow rate of water into the tank, q_i , is constant. Use the information given in Figure P32.13 to decide whether the amount of water in the tank increases, decreases, or remains the same. If it changes, how much time is required to completely empty or fill the tank, as the case may be?

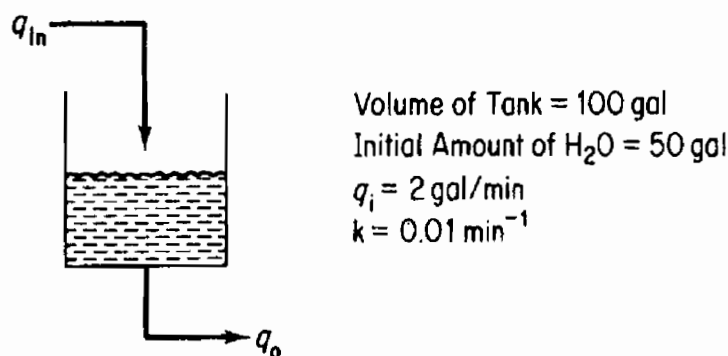
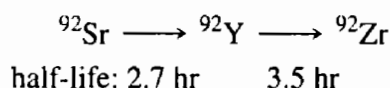


Figure P32.13

- 32.14** A stream containing a radioactive fission product with a decay constant of 0.01 hr^{-1} (i.e., $dn/dt = 0.01 n$), is run into a holding tank at the rate of 100 gal/hr for 24 hr. Then the stream is shut off for 24 hr. If the initial concentration of the fission product was 10 mg/liter and the tank volume is constant at 10,000 gal of solution (owing to an overflow line), what is the concentration of fission product:
- At the end of the first 24-hr period?
 - At the end of the second 24-hr period?

What is the maximum concentration of fission product? Assume complete mixing in the tank.

- 32.15** A radioactive waste that contains 1500 ppm of ^{92}Sr is pumped at the rate of $1.5 \times 10^{-3} \text{ m}^3/\text{min}$ into a holding tank that contains 0.40 m^3 . ^{92}Sr decays as follows:



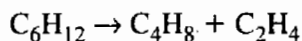
If the tank contains clear water initially and the solution runs out at the rate of $1.5 \times 10^{-3} \text{ m}^3/\text{min}$, assuming perfect mixing:

- What is the concentration of Sr, Y, and Zr after 1 day?
- What is the equilibrium concentration of Sr and Y in the tank?

The rate of decay of such isotopes is $dN/dt = -\lambda N$, where $\lambda = 0.693/t_{1/2}$ and the half-life is $t_{1/2}$. N = moles.

- 32.16** A tank contains 3 m^3 of pure oxygen at atmospheric pressure. Air is slowly pumped into the tank and mixes uniformly with the contents, an equal volume of which is forced out of the tank. What is the concentration of oxygen in the tank after 9 m^3 of air has been admitted?

- 32.17** Suppose that an organic compound decomposes as follows:



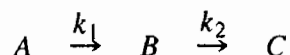
If 1 mol of C_6H_{12} exists at $t = 0$, but no C_4H_8 and C_2H_4 , set up equations showing the moles of C_4H_8 and C_2H_4 as a function of time. The rates of formation of C_4H_8 and C_2H_4 are each proportional to the number of moles of C_6H_{12} present.

- 32.18** A large tank is connected to a smaller tank by means of a valve. The large tank contains N_2 at 690 kPa while the small tank is evacuated. If the valve leaks between the two tanks and the rate of leakage of gas is proportional to the pressure difference between the two tanks ($p_1 - p_2$), how long does it take for the pressure in the small tank to be one-half its final value? The instantaneous initial flow rate with the small tank evacuated is 0.091 kg mol/hr.

	Tank 1	Tank 2
Initial pressure (kPa)	700	0
Volume (m^3)	30	15

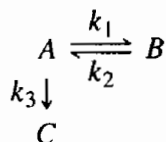
Assume that the temperature in both tanks is held constant and is 20°C.

- 32.19** The following chain reactions take place in a constant-volume batch tank:



Each reaction is first order and irreversible. If the initial concentration of A is C_{A_0} and if only A is present initially, find an expression for C_B as a function of time. Under what conditions will the concentration of B be dependent primarily on the rate of reaction of A ?

- 32.20** Consider the following chemical reactions in a constant-volume batch tank:



All the indicated reactions are first order. The initial concentration of A is C_{A_0} , and nothing else is present at that time. Determine the concentrations of A , B , and C as functions of time.

- 32.21** Tanks A , B , and C are each filled with 1000 gal of water. See Figure P32.21. Workers have instructions to dissolve 2000 lb of salt in each tank. By mistake, 3000 lb is dissolved in each of tanks A and C and none in B . You wish to bring all the compositions to within 5% of the specified 2 lb/gal. If the units are connected $A-B-C-A$ by three 50-gpm pumps,
- Express the concentrations C_A , C_B , and C_C in terms of t (time).
 - Find the shortest time at which all concentrations are within the specified range. Assume the tanks are all well mixed.

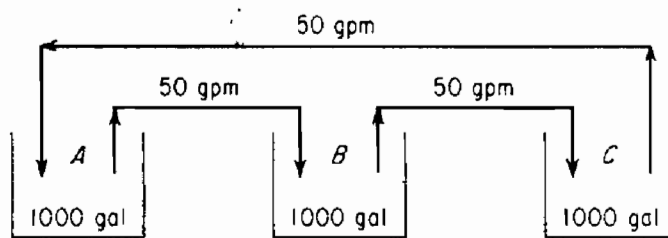


Figure P32.21

- 32.22** Determine the time required to heat a 10,000-lb batch of liquid from 60°F to 120°F using an external, counterflow heat exchanger having an area of 300 ft². Water at 180°F is used as the heating medium and flows at a rate of 6000 lb/hr. An overall heat transfer coefficient of 40 Btu/(hr)(ft²)(°F) may be assumed; use Newton's law of heating. The liquid is circulated at a rate of 6000 lb/hr, and the specific heat of the liquid is the same as that of water (1.0). Assume that the residence time of the liquid in the external heat exchanger is very small and that there is essentially no holdup of liquid in this circuit.
- 32.23** A ground material is to be suspended in water and heated in preparation for a chemical reaction. It is desired to carry out the mixing and heating simultaneously in a tank equipped with an agitator and a steam coil. The cold liquid and solid are to be added continuously, and the heated suspension will be withdrawn at the same rate. One method of operation for starting up is to (1) fill the tank initially with water and solid in the proper proportions, (2) start the agitator, (3) introduce fresh water and solid in the proper proportions and simultaneously begin to withdraw the suspension for reaction, and (4) turn on the steam. An estimate is needed of the time required, after the steam is turned on, for the temperature of the effluent suspension to reach a certain elevated temperature.
- Using the nomenclature given below, formulate a differential equation for this process. Integrate the equation to obtain n as a function of B and ϕ (see nomenclature).
 - Calculate the time required for the effluent temperature to reach 180°F if the initial contents of the tank and the inflow are both at 120°F and the steam temperature is 220°F. The surface area for heat transfer is 23.9 ft², and the heat transfer coefficient is 100 Btu/(hr)(ft²)(°F). The tank contains 6000 lb, and the rate of flow of both streams is 1200 lb/hr. In the proportions used, the specific heat of the suspension may be assumed to be 1.00.

If the area available for heat transfer is doubled, how will the time required be affected? Why is the time with the larger area less than half that obtained previously? The heat transferred is $Q = UA(T_{\text{tank}} - T_{\text{steam}})$.

Nomenclature

- W = weight of tank contents, lb
 G = rate of flow of suspension, lb/hr
 T_s = temperature of steam, °F

T = temperature in tank at any instant, perfect mixing assumed, °F

T_0 = temperature of suspension introduced into tank; also initial temperature of tank contents, °F

U = heat-transfer coefficient, Btu/(hr)(ft²)(°F)

A = area of heat-transfer surface, ft²

C_p = specific heat of suspension, Btu/(lb)(°F)

t = time elapsed from the instant the steam is turned on, hr

n = dimensionless time, Gt/W

B = dimensionless ratio, UA/GC_p

ϕ = dimensionless temperature (relative approach to the steam temperature)
 $(T - T_0)/(T_s - T_0)$

32.24 Consider a well-agitated cylindrical tank in which the heat transfer surface is in the form of a coil that is distributed uniformly from the bottom of the tank to the top of the tank. The tank itself is completely insulated. Liquid is introduced into the tank at a uniform rate, starting with no liquid in the tank, and the steam is turned on at the instant that liquid flows into the tank.

(a) Using the nomenclature of Problem 32.23, formulate a differential equation for this process. Integrate the differential equation to obtain an equation for ϕ as a function of B and f , where f = fraction filled = W/W_{filled} .

(b) If the heat transfer surface consists of a coil of 10 turns of 1-in.-OD tubing 4 ft in diameter, the feed rate is 1200 lb/hr, the heat capacity of the liquid is 1.0 Btu/(lb)(°F), the heat transfer coefficient is 100 Btu/(hr)(°F)(ft²) of covered area, the steam temperature is 200°F, and the temperature of the liquid introduced into the tank is 70°F, what is the temperature in the tank when it is completely full? What is the temperature when the tank is half full? The heat transfer is given by $Q = UA(T_{\text{tank}} - T_{\text{steam}})$.

32.25 A cylindrical tank 5 ft in diameter and 5 ft high is full of water at 70°F. The water is to be heated by means of a steam jacket around the sides only. The steam temperature is 230°F, and the overall coefficient of heat transfer is constant at 40 Btu/(hr)(ft²)(°F). Use Newton's law of cooling (heating) to estimate the heat transfer. Neglecting the heat losses from the top and the bottom, calculate the time necessary to raise the temperature of the tank contents to 170°F. Repeat, taking the heat losses from the top and the bottom into account. The air temperature around the tank is 70°F, and the overall coefficient of heat transfer for both the top and the bottom is constant at 10 Btu/(hr)(ft²)(°F).

APPENDIX A

ANSWERS TO THE SELF-ASSESSMENT TESTS

Chapter 1

Section 1.1

Q1. (c)

Q2. (a)

Q3. Derived

Q4. No, too close together

P2. (a), (d), (e) are correct

Section 1.2

Q1. (a) – (e) yes; (f) and (g) no; (h) and (i) no; (j) no

Q2. The dimensions are not the same.

Q3. One way is to make the arguments dimensionless. Also look at Discussion Problem 1.

P1. Change units to get 101 cm.

P2. Change units to get 9 ft.

P3. 1.5 m

P4. 8 (ft)(lb)

Section 1.3

Q1. A conversion factor in the American Engineering system of units.

Q2. Yes.

Q3. Lb_f is force and lb_m is mass, and the dimensions are different.

Q4. The unit is not legal in SI.

- Q5.** In SI the magnitudes of many of the units are scaled on the basis of 10, but not in AE. Consequently, the units are often ignored in making conversion in SI.
- Q6.** (a) 1 lb_f in the AE system of units; (b) yes; (c) no
- Q7.** 1000 kg
- P1.** 1, dimensionless
- P2.** 5.38 hr
- P3.** 0.14 (ft) (lb_f)
- P4.** (a) 5.96 kg/m; (b) 16.0 kg/(m³)(s)
- P5.** 1.06×10^{-3} lb_m/(ft)(s)
- P6.** 0.15 ft³
- P7.** 4.16×10^{-3} m³

Section 1.4

- Q1.** All additive terms on the righthand side of an equation must have the same dimensions as those on the lefthand side.
- Q2.** All of the units cancel out.
- Q3.** Yes
- Q4.** (a) Divide by the radius or diameter; (b) divide by the total time to empty the tank, or by a fixed unit of time
- P1.** c is dimensionless
- P2.** A has the same units as k ; B has the units of T

Section 1.5

- Q1.** The relative error may be too large.
- Q2.** Retain extra digits in the calculations.
- Q3.** No
- P1.** (a) in $3.0 - 2$; (b) in $23 - 2$; (c) in $0.353 - 3$; (d) in $1,000 - 1$; (e) in $1,000. - 4$; (f) $1,000.0 - 5$
- P2.** (a) $5760 - 3$ significant figures; (b) $2.22 - 3$ significant figures
- P3.** 1,380 gal/hr (3 significant figures in 87.0)
- P4.** 10,000 yen has at least 5 significant figures even though no decimal is shown. The given conversion rate has at least 3 significant figures (in reality more). The answer should be at least \$78.0.
- P5.** 74.8

Section 1.6

- Q1.** Probably, if you are careful to enter the correct numbers and carry out the correct operations.
- Q2.** (a) Wait some time, and redo the calculations without looking at the original solution; (b) ask a friend to do the calculations, and compare answers; (c) if in a text, see if the answer is provided
- Q3.** Look up the density of solid CaCl_2 , calculate the mass, and compare with 4.72 lb, or start with 4.72 and convert to grams. Multiply the grams by 2, and see if you get twice the pounds.
- P1** Some error exists as **B** is not retrieved.

Chapter 2

Section 2.1

- Q1.** (a) T; (b) T; (c) T
- Q2.** 60.05
- P1.** (a) 7010 g; (b) 2.05 g mol; (c) 7010 lb; (d) 2.05 lb mol
- P2.** 0.123 kg mol NaCl/kg mol H_2O
- P3.** 1.177 lb mol

Section 2.2

- Q1.** No
- Q2.** (a) T; (b) T; (c) T
- Q3.** 13.6 g/cm^3
- Q4.** 1000 kg/m^3
- P1.** $0.5 \text{ m}^3/\text{kg}$
- P2.** 46.2 lb
- P3.** Measure the mass of water (should be about 500g) and add it to 50 g. Measure the volume of the solution (will not be 450 mL). Divide the mass by the volume.

Section 2.3

- Q1.** The statement means that the density at 10°C of liquid HCN is 1.2675 times the density of water at 4°C .

Q2. (a) F—the units differ; (b) T; (c) T; (d) F

P1. 0.79389 g/cm³ (assuming the density of water is also at 60°F)

P2. 8.11 ft³

P3. 2.00 ft³

P4. 870 kg HNO₃/m³ solution

Section 2.4

P1. 132 min

P2. 0.654 kg mol/hr

Section 2.5

P1. 9

P2. SO₂

P3. 14.8 kg

P4. O₂ 0.62; SO₂ 0.19; SO₃ 0.19

Section 2.6

Q1. Mass

Q2. Neither (they are fractions of however the emissions are reported)

Q3. (a) T; (b) T; (c) T

P1. (d)

P2. 72.17 lb

P3. (a) C₄: 0.50, C₅: 0.30, C₆: 0.20; (b) C₄: 0.57, C₅: 0.28, C₆: 0.15; (c) C₄: 57, C₅: 28, C₆: 15; (d) 66.4 kg/kg mol

Section 2.7

Q1. For gases but not for liquids or solids.

Q2. No

Q3. 0.001

Q4. 1000

Q5. No (4 times)

Q6. No (80% less; can't be less than 100%)

P1. 12,000 mg/L

P2. Report 1400 FC/100 mL

P3. 1.68×10^{-3} ppm

Chapter 3

Q1. See text

Q2. For convenience or to simplify the calculations.

Chapter 4

Q1. (a) 0°C and 100°C; (b) 32°F and 212°F

Q2. $\Delta^{\circ}\text{F} (1.8) = \Delta^{\circ}\text{C}$

Q3. Yes. Yes.

Q4. $93.2 + 0.186 T_{\text{of}}$

Q5. Immerse in ice-water bath and mark 0°C. Immerse in boiling water and mark 100°C. Interpolate between 0°C and 100°C in desired intervals.

Q6. (a) 1°C; (b) 1°C; (c) 1 Δ°C

P1.

°C	°F	K	°R
−40.0	−40.0	233	420
25.0	77.0	298	537
425	796	698	1256
−234	−390	38.8	69.8

Chapter 5

Section 5.1

Q1. Both pots will hold the same amount of coffee if the diameters of the pots and the levels of the spouts are the same.

Q2. 3 is the highest pressure; next are 1 and 2, which are the same; and 4 is last. The decisions are made by dividing the weight of water by the base area.

Section 5.2

- Q1.** All are true
Q2. Gauge pressure + barometric pressure = absolute pressure
Q3. See text
Q4. Barometric pressure – vacuum pressure = absolute pressure
P1. (a) 15.5; (b) 106.6; (c) 1.052; (d) 35.6
P2. (A) Gauge pressure; (B) barometric pressure, absolute pressure; (C) 50 in. Hg
P3. In the absence of a barometric pressure value, assume 101.3 kPa. The absolute pressure is 61.3 kPa.

Section 5.3

- Q1.** Both are true
P1. The Hg is static. (a) 3.21 kPa; (b) 3.47 kPa
P2. 63.8 cm Hg

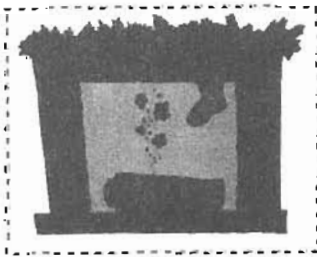
Chapter 6

Section 6.1

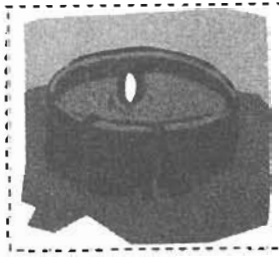
- Q1.** The conservation of mass focuses on the invariance of material in a system, whereas a material balance focuses on ensuring that the flows in and out of the system along with the material in the system can be equated.
Q2. See text
P1. A system that you pick will be somewhat arbitrary, as will be the time interval for analysis, but (a) and (c) can be closed systems (ignoring evaporation), and (b) open.



Teapot



Hearth



Swimming Pool

Section 6.2

Q1. Yes

Q2. On a very short time scale when all of the valves are closed—closed system; on a longer time scale—open system.

P1. See Q2 for the concept

P2. (a) Closed; (b) open (flow); (c) open (flow); (d) open (flow).

P3. (a) Water, air if you pick the inside of the tank as the system; (b) air, the tank shell itself and insulation, and the heating element if gas (an electric heating element would probably be inside the tank; (c) closed until water is used, then open.

Section 6.3

Q1. Not necessarily—accumulation can occur

Q2. See text

Q3. Yes; depletion

Q4. No reaction (a) closed system, or (b) flow of a component in and out are equal.

Q5. In an unsteady-state system, the state of the system changes with time, whereas with a steady-state system, it does not.

Q6. A transient process is an unsteady-state process—see Q5.

P1. Based on the time interval: (a) unsteady for short times; (b) unsteady during flushing, steady between flushings; (c) unsteady during the operation of the car, steady otherwise; (d) unsteady during start-up and shut down, steady during normal operation.

Section 6.4

Q1. Yes

Q2. Yes

P1. 7,740

P2. 1.49×10^{-3} mg/L

Section 6.5

Q1. See text

Q2. (a) Accumulation; (b) flow in and out; (c) generation and consumption

Section 6.6

Q1. None

Q2. A flow in occurs

Q3. None, except in a flow process, usually flows occur both in and out

P1. (a) Neither; (b) neither; (c) probably batch; (d) semibatch; (e) neither

P2. 1

Chapter 7

Section 7.2

Q1. A solution means a (possibly unique) set of values for the unknowns in a problem that satisfies the equations formulated in the problem.

Q2. (a) one; (b) three; (c) three

Q3. Linear equations are independent if the vectors formed from the row coefficient in the equation are independent (see Appendix L1). For nonlinear equations, no simple definition exists.

Q4. Delete nonpertinent equations, or find additional variables not included in the analysis.

Q5. The sum of the mass or mole fraction in a stream or inside a system is unity.

Q6. Obtain more equations or specifications, or delete variables of negligible importance.

P1. (a) Two; (b) two of these three: acetic acid, water, total; (c) two; (d) feed of the 10% solution (say F) and mass fraction ω of the acetic acid in P ; (e) 14% acetic acid and 86% water

P2. Not for a unique solution because only two of the equations are independent.

P3. F , D , P , ω_{D2} , ω_{P1}

P4. Three unknowns exist. Because only two independent material balances can be written for the problem, one value of F , D , or P must be specified to obtain a solution. Note that specifying values of ω_{D2} or ω_{P1} will not help.

Chapter 8

Section 8.2

Q1. (a) T; (b) F; (c) T; (d) F

Q2. When they are not independent.

- P1.** 33.3 kg
P2. 178 kg/hr
P3. (a) 28% Na₂SO₄; (b) 33.3
P4. salt: 0.00617; oil: 0.99393

Chapter 9

Section 9.1

Q1. When writing a chemical equation, you can use the stoichiometric ratios of two species, but 1 mol MnO₄⁻ is not equal to 5 mol Fe²⁺ and their ratio is not equal to a dimensionless 1. That line in the solution is wrong.

- P1.** (a) $\text{C}_9\text{H}_{18} + \frac{27}{2}\text{O}_2 \rightarrow 9\text{CO}_2 + 9\text{H}_2\text{O}$; (b) $4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$

- P2.** 3.08
P3. 323
P4. No

Section 9.2

- Q1.** ξ (xisi)
Q2. Reactant present in the least stoichiometric quantity.
Q3. All other reactants than the limiting reactant.
Q4. For a species in

$$\text{Open system: } \xi = \frac{n_{\text{out}, i} - n_{\text{in}, i}}{v_i} \quad \text{Closed system: } \xi = \frac{n_{\text{final}, i} - n_{\text{initial}, i}}{v_i}$$

- P1.** (a) 1, (b) 1, (c) the same, (d) The extent of reaction depends on the reaction equation as a whole and not on one species in the equation.
P2. (a) CaCO₃: 43.4%, CaO: 56.4%; (b) 0.308
P3. (a) H₂SO₄; (b) 79.2%; (c) 0.89
P4. (a) C₂H₆ (the hydrogen is from reaction No.2, not the feed); (b) None; (c) fraction conversion = 0.184; (d) 1.22; 0.45 (e) based on reactant in the feed: 0.45, based on reactant consumed: 0.84, based on theory: 0.50; (f) reaction (a) is 33 mol reacting and reaction (b) is 13.5 mol reacting, both based on 100 mol product.

Chapter 10

Section 10.1

- Q1.** (a) T; (b) T if you are thinking of C as an element but F if you are thinking of C as a compound because the exit product contains CO_2 , not C; (c) F (the reaction may be reversible and the compound changes in going through the process, or several reactions may occur with the effect of no net change in the compound).
- Q2.** See text
- Q3.** The value of the extent of reaction or conversion, or data to calculate one of the two values.
- Q4.** Total mass: Yes, Yes
Total moles: Yes, No
Mass of a pure compound: Yes, No
Moles of a pure compound: Yes, No
Mass of an atomic species: Yes, Yes
Moles of an atomic species: Yes, Yes
- Q5.** See Equation (10.5)
- P1.** 186 kg
- P2.** 887 lb
- P3.** (a) $\text{C}_{12}\text{H}_{14} = 139 \text{ mol/hr}$; (b) $\text{H}_2\text{O} = 453 \text{ mol/hr}$; (c) $\text{CO} = 347 \text{ mol/hr}$; (d) $\text{H}_2 = 640 \text{ mol/hr}$; (e) $\text{C}_6\text{H}_{14} = 53.3 \text{ mol/hr}$

Section 10.2

- Q1.** No. If the units of each term are mass, dividing each term by the MW makes the units moles, and the reverse.
- Q2.** The degrees of freedom should be the same if the problem is properly formulated.
- Q3.** (a) Get the rank of the coefficient matrix, (b) put the equations in an equation solver, or (c) just examine them for possible redundancy.
- Q4.** No
- P1.** Two
- P2.** Three
- P3.** See the answers to the problems for the Self-Assessment Test in Section 10.1.

Section 10.3

Q1. Orsat (dry basis) does not include the water vapor in the analysis.

Q2. SO_2 is not included in the analysis.

Q3. See text

Q4. Yes

Q5. More

Q6. (a) T; (b) T; (c) F; (d) F

P1. 4.5%

P2. 9.1% CO_2 , 8.9% O_2 , 82.0% N_2

P3. 1

P4. (a) 252; (b) 1.063; (c) 2.31; (d) 33.8%

P5. 0.81

Chapter 11

Q1. Yes

Q2. Yes, even if the equipment is continuous.

Q3. It does not have to, but usually it is useful to do so.

Q4. No, if the degrees of freedom are calculated correctly.

P1. Assume that the compositions in the figure are mass fractions. Then:

	lb	mass fraction
Toluene	396	0.644
Benzene	19.68	0.032
Xylene	200	0.325

P2. 863 lb air/lb S

	Converter	Burner
SO_2	0.5%	9.5%
SO_3	9.4	—
O_2	7.4	11.5
N_2	82.7	79.0

P3. (a) 1.14; (b) 2240 lb; (c) 9.9%

Chapter 12

Section 12.1

Q1. A recycle stream is used to improve the performance and economics of a process.

Q2. No, if separation occurs before the recycle occurs.

P1. 2

P2. 5

Section 12.2

Q1. We assumed the process(es) was in the steady state for the problems.

Q2. Under unsteady-state conditions, particularly during start-up and shutdown, or during changes in the steady-state operating conditions.

Q3. Essentially all systems; see text for some examples.

Q4. Yes

P1. \$2250

P2. (a) 591 lb/hr; (b) 409 lb/hr; (c) 0.55

P3. (a) ratio = 3000 kg of recycle/hr and feed = 7000 kg/hr; (b) air = 85,100 kg/hr

P4. (a) benzene extracted: $P = 625$ lb/hr; (b) raffinate produced: $R = 3,281$ lb/hr

Section 12.3

Q1. The stoichiometric ratio

Q2. All true

Q3. (1) Recovery of catalyst; (2) to dilute a component in a process stream; (3) to control a process variable; (4) eliminate discharge of a pollutant; (5) save money.

P1. (a) mol/hr $C_4H_6 = 37.5$ and $F = 50.5$ mol/hr; (b) 0.65

P2. (a) 960 kg/hr; (b) 3659 kg/hr

P3. (a) 1570 kg/hr; (b) 243 kg/hr

Section 12.4

Q1. Bypassing is a stream that skips some intermediate processing unit (or system), and joins the process downstream.

Q2. (a) T; (b) F; (c) F

- Q3.** Not necessarily. A purge is considered a stream that removes a small amount of a component to prevent it from building up in the system. A waste stream usually contains a large amount of a component.
- P1.** (a) 890 recycled and 3.2 purged; (b) 9.2% conversion (errors can be caused by loss of significant figures)
- P2.** (a) 1.49 mol/hr; (b) Cl_2 : 0.658; C_2H_4 : 0.338; $\text{C}_2\text{H}_4\text{Cl}_2$: 0.0033

Chapter 13

Section 13.1

- Q1.** $PV = nRT$
- Q2.** T : absolute temperature in degrees; p : absolute pressure in mass/(length)(time)²; V : (length)³/mole; n : mole; R : (mass)(length)²/(time)²(mole)(degree)
- Q3.** See text
- Q4.** To get the mass density, convert moles to mass and divide by volume.
- Q5.** Yes
- Q6.** No
- Q7.** Yes
- P1.** 1883 ft³
- P2.** 2.98 kg
- P3.** 1.32
- P4.** 28.3 m³/hr
- P5.** 38.1 kg/m³
- P6.** 1.02
- P7.** 140°F

Section 13.2

- Q1.** Lower
- Q2.** Yes
- Q3.** The pressure in the balloon may go up slightly, in which case the partial pressure of the components of the gas increase.
- Q4.** No

- P1.** (a) N_2 : 0.28 psia; CH_4 : 10.9 psia; C_2H_6 : 2.62 psia. The volume fractions are the same as the mole fractions. Divide the mole percents by 100.
P2. Assuming the temperature is still 120°F : (a) 11.12 psia; (b) 0.28 psia

Section 13.3

- Q1.** No effect, except that the amount of material can be specified in terms of temperature, pressure, and volume
Q2. It may or may not. It may if p , V , and T are given so that an amount of material is specified.
P1. (a) $2,735 \text{ ft}^3/\text{hr}$; (b) $5,034 \text{ ft}^3/\text{hr}$; (c) $22,430 \text{ ft}^3/\text{hr}$; (d) $30,975 \text{ ft}^3/\text{hr}$, all at the exit temperature and pressure
P2. $118,400 \text{ ft}^3/\text{hr}$
P3. 791 kPa

Chapter 14

- Q1.** $\hat{V}_{c_i} = RT_c/p_c$; it can be used as a different parameter on the compressibility charts when a value of p or T is not known.
Q2. All are true except (f).
Q3. It means that z is a function of T_r and p_r
Q4. 1
P1. (a) Yes; (b) Yes; (c) No
P2. (a) No; (b) 5.0 ft^3 ; (c) 2.3 ft^3
P3. 1.65 kg
P4. 14.9 atm
P5. 262 atm

Chapter 15

- Q1.** The equation is explicit in p or T but implicit in V .
Q2. (1) A phase change can occur from a gas to a liquid; (2) near the critical region the properties require a very complex curvature for any function, and also at low temperature and high pressure; (3) the equation has to be used to predict other physical properties.
Q3. Low temperature and high pressure.

Q4. In general, yes, but not always

Q5. Decide on the form of the function used to fit the data, and then use a statistical program to estimate the values of the coefficients in the function.

Q6. Multiply by \hat{V} or V and divide by RT

Q7. b is m^3 ; a is $(\text{K})^{0.5}(\text{m})^6(\text{kPa})$

P1.

Virial

$$Z = 1 + B'p + \dots \quad Z = 1 + \frac{B}{\hat{V}} + \dots$$

van der Waals

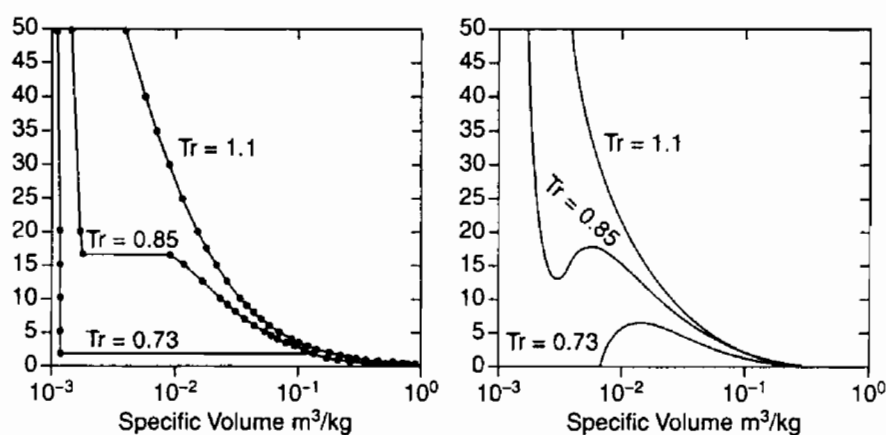
$$Z = 1 + \frac{b}{\hat{V} - b} - \frac{a^2}{\hat{V}RT}$$

Peng-Robinson

$$Z = 1 + \frac{b}{\hat{V} - b} - \frac{a\alpha}{RT} \left[\frac{\hat{V}}{\hat{V}^2 + 2b\hat{V} - b^2} \right]$$

P2. See above

P3. See below



P4 All values in cm^3/g . (a) 7.81; (b) 2.1 to 3.7 (depends on how the value of z is selected); (c) 3.91; (d) 4.13

P5. $V = 0.60 \text{ ft}^3$

P6. 314 K

P7. (a) 50.7 atm; (b) 34.0 atm

P8. $0.315 \text{ m}^3/\text{kg mol}$

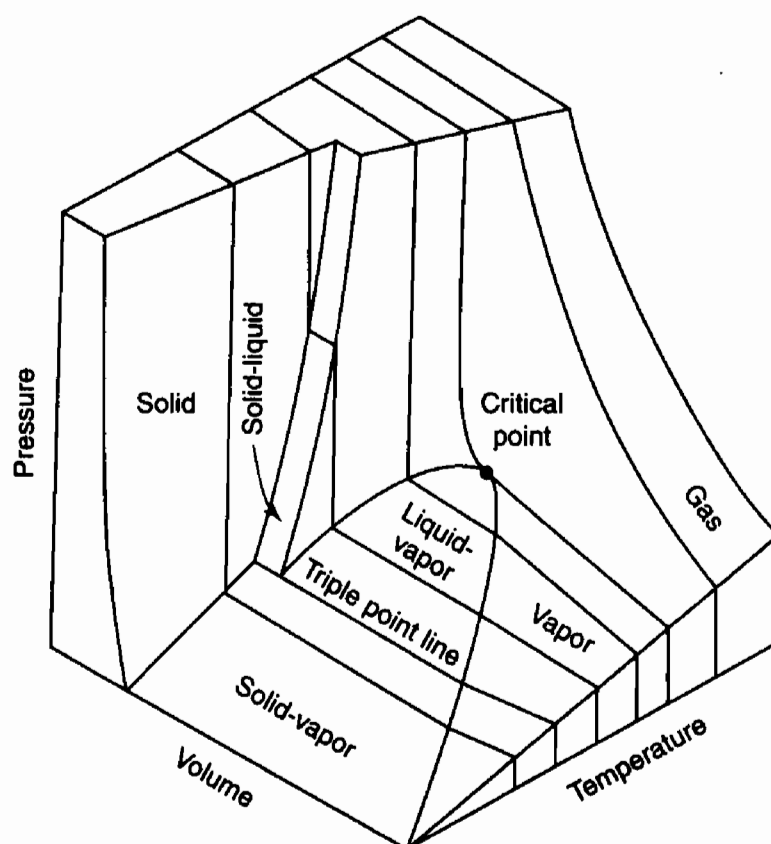
Chapter 16

Section 16.1

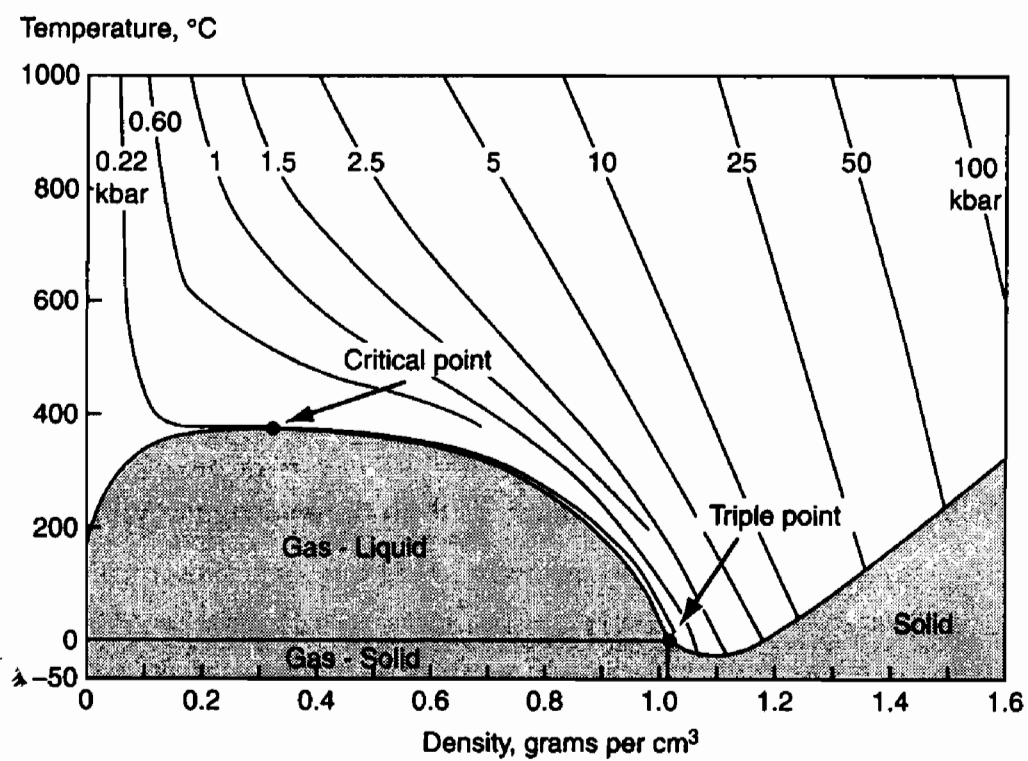
- Q1.** No. Copper sulfate would decompose and not form a gas of copper sulfate molecules.
- Q2.** (a) High altitude where the atmospheric pressure is less than 12.75 psia so that it could be compressed and subsequently expanded below the triple point, causing solidification. (b) Ship it under vacuum cooled. (c) Allow the ambient conditions to heat the solid and adjust the pressure so that the system is above the triple point at a state where liquid can form.
- Q3.** (a) Yes. (b) No, it sublimates at room temperature.
- Q4.** The point representing ambient temperature and pressure falls below the liquid region—only solid and vapor exist in equilibrium.
- Q5.** The pressure of the water vapor inside the pot relative to an open pot is higher, and hence the temperature is higher so that food cooks faster.
- P1.** If equilibrium is maintained, the pressure is the vapor pressure of 610 mm Hg.
- P2.** See Figures 16.2 and 16.3.

Section 16.2

- Q1.** Run at as low a temperature as possible to reduce the lead vapor pressure, and condense the lead vapor at a much lower temperature to reduce the emissions to the atmosphere.
- Q2.** A form similar to the Antoine equation will do.
- Q3.** Yes
- Q4.** Yes, if you use another substance as the reference substance.
- P1.** Ice at its vapor pressure changes to liquid water at 32°F (0°C) and 0.0886 psia (0.6113 kPa). Then liquid and vapor exist (at equilibrium) as the temperature goes up to 250°F.
- P2.** (a) 75 psia; (b) it sublimates
- P3.** Experimental value is 219.9 mm Hg; the calculated value is 220.9 mm Hg.
- P4.** 80.1°C
- P5.** Look at Figure 16.7.
- P6.** See below



P7. See below



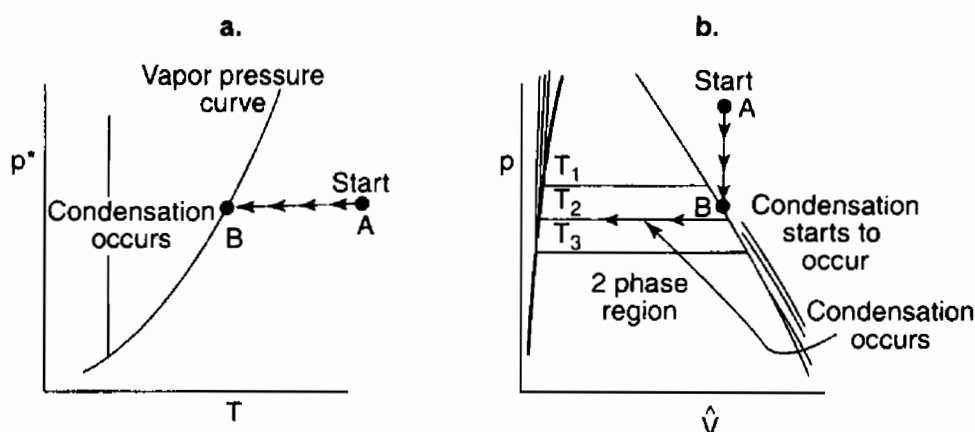
Chapter 17

Section 17.1

- Q1.** At equilibrium the partial pressure of the condensable component in the gas equals the vapor pressure of the condensable component.
- Q2.** (a) Yes; (b) Yes
- Q3.** (a) Both gas; (b) some liquid water with the residuum gas; (c) both gas; (d) some liquid water with the residuum gas
- Q4.** Dilute it with inert gas.
- Q5.** At saturation
- Q6.** No
- P1.** 0.0373
- P2.** 4.00 lb
- P3.** Water vapor is 0.025 and air is 0.975
- P4.** 1.4% benzene has a pressure of 1.4 kPa (10.6 mm Hg) and a dew point of -11°C ; 8.0% has a pressure of 7.9 kPa (60.8 mm Hg) and a dew point of 15°C . This fixes the temperature range for an explosion. The answer is possibly.
- P5.** 7.2 L at SC

Section 17.2

- Q1.** No
- Q2.** To dilute any SO_3 (and perhaps SO_2) formed that would corrode metal surfaces and also to eliminate CO from the stack gas.
- Q3.** No, the dew point is a temperature, not a pressure.
- Q4.** Reduce the temperature, raise the pressure, reduce the volume.
- Q5.** Yes, see the answers to Q4
- P1.** 21°C ; benzene
- P2.** 2.69 lb in the oxygen cylinder and 5.37 lb in the hydrogen cylinder

P3. and P4.**Section 17.3****Q1.** No.**Q2.** (a) No; (b) Yes; (c) No

Q3. The pressure will drop in the bell jar until eventually the vapor pressure for water is reached at ambient temperature, and then the water will definitely boil (some indication of boiling may occur prior to this state). Then the pressure will remain constant at the vapor pressure until all of the water has vaporized. Note: If air is in the bell jar to start with, how much air remains during the process affects the total pressure.

P1. 72.7 L or 2.56 ft³**P2.** 5190 lb/hr**P3.** A very, very slight increase—about 0.07%.**P4.** 536 m³ at 100 kPa and 21°C**Chapter 18****Section 18.1****Q1.** molal saturation = $(p^*_{\text{vapor}})(\mathcal{R}S)/p_{\text{vapor-free gas}}$ **Q2.** $\mathcal{H} = (p^*_{\text{H}_2\text{O}})(\mathcal{R}\mathcal{H})(18)/(p_{\text{dry air}})(29)$ **Q3.** Yes, for 0 and also, unlikely, when $p^*_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}} = p_{\text{BDAir}}$ **Q4.** (a) $\mathcal{R}\mathcal{H} = 1.00$; (b) $\mathcal{H} = (p^*/p_{\text{dry air}})(18/29)$ **P1.** 0.063**P2.** 69.8%**P3.** 86% $\mathcal{R}\mathcal{H}$

P4. 15.3°C

P5. (a) 43.6%; (b) 0.0136 mol toluene/mol air; (c) 0.043; (d) 1.34%

Section 18.2

P1. 40°C

P2. 71% water

P3. 94% \mathcal{RH}

Chapter 19

Section 19.1

Q1. (a) Any of p , T , \hat{V} , c , ρ , etc.; (b) Any of V , m , n , etc.

Q2. All true

Q3. 1 phase: 2; two phases: 1; 3 phases: 0

Q4. No

P1. (a) 2; (b) 2; (c) 0

P2. No (5 phases involved: 2 solid, 2 liquid, 1 gas)

Section 19.2

Q1. Raoult's law accurately represents the vapor-liquid equilibrium for only a few systems.

Q2. Henry's law for a gas dissolved in a solvent; Raoult's law for the solvent in ideal solutions.

Q3. Butane

Q4. Yes, because the solution acts as an ideal solution.

P1. 114.5°C

P2. (a) $y_{Bz} = 1$, $x_{Bz} = 1$; (b) $y_{Bz} = 0$, $x_{Bz} = 0$; (c) $y_{Bz} = 0.453$, $x_{Bz} = 0.256$

P3. $y_{Bz} = 0.52$, $x_{Bz} = 0.30$, $T = 97.7^\circ\text{C}$

Section 19.3

P1. (a) 190 psia; (b) $C_2H_6 = 0.0677$, $C_3H_8 = 0.660$, $i\text{-}C_4H_{10} = 0.2415$, $n\text{-}C_4H_{10} = 0.0308$

P2. $L/F = 0.75$

Section 21.2-6**Q1.** Liquid**Q2.** Vapor**P1.**

$$(a) \hat{H}_2 - \hat{H}_1 = \int_{p_1}^{p_2} \left[\hat{U} - T \left(\frac{\partial \hat{V}}{\partial T} \right)_p \right] dp$$

$$(b) \hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT + \int_{p_1}^{p_2} \hat{V} dp$$

$$(c) \hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT$$

P2. Neither because the enthalpy change is the same by either path.**P3.** See the answer to P1 (b) with constant volume**Chapter 22****Section 22.1****Q1.** Yes for the system plus the surroundings, no for either one individually.**Q2.** Conservation means no overall change; a balance shows the details of changes within the prescribed no overall change.**Q3.** Not in this book**Section 22.2****Q1.** All false except 4 and 5, which are true.**Q2.** No**Q3.** (a) The truck; (b) open (air in, gases out), and possibly unsteady state if the truck is decelerating, otherwise steady state.**Q4.** Final state minus initial state**P1.** (a) -30 kJ; (b) -35 kJ**P2.** 200 Btu**P3.** Assume $Q = 0$. Mass hot water/mass cold water = 2

Section 22.3

Q1. All true

Q2. The question is ill posed, because if the system is in the steady state, no change in internal energy occurs.

Q3. $\Delta KE = \Delta PE = \Delta U = 0$

P1. Zero

Section 22.4

Q1. No, usually they operate in the steady state, but not always.

Q2. Yes

Q3. (a) T; (b) possibly, depending on the location above a reference plane; (c) T; (d) T; (e) F

Q4. All the other terms in the equation are eliminated by being zero, equal, or negligible.

Q5. No, no flow term exists in the equation.

Q6. Yes

Q7. Probably not because ΔE apparently is zero and ΔH represents flow (although it might apply in special cases to a closed system).

Q8. No

P1. (a) No term dropped; (b) $Q = 0$; (c) $\Delta KE = 0$; (d) no term dropped

P2. $\Delta KE = \Delta PE = 0$ inside the system, $Q = W = 0$. And $\Delta KE = \Delta PE = 0$ for the flow in and out of the system.

P3. $Q = (445.6)(1.8) - 337.75(0.8) - 560.51(1.0) = -28.6 \text{ kJ}$

Section 22.5

Q1. (a) If done on the surroundings, F; (b) F (it is out minus in); (c) T; (d) T; (e) F

Q2. (1) Insulated system, (2) no temperature difference between system and surroundings, (3) it is negligible relative to the other terms in the equation.

Q3. ΔE

Q4. Temperature and pressure (and composition)

Q5. (a) KE : no velocity of fluid flow, $KE_{in} = KE_{out}$, KE is negligible relative to other terms; (b) PE : no height difference exists for streams above the reference plane, $PE_{in} = PE_{out}$, PE is negligible relative to other terms

P1. Result is $Q = \Delta H$

P2. 423 kJ

P3. (a) -5.03 MW; (b) 39%

Chapter 23

Section 23.1

Q1. (a) F (it is a function of T); (b) T; (c) F (it is for melting)

Q2. See text

Q3. Tradition

P1. By using the Watson equation 13.445 kJ/g mol (the experimental value is 13.527 kJ/g mol)

P2. 105 kJ/g

P3. $Q = -219.7$ kJ

Section 23.2

Q1. All false except (b), which is true

Q2. Probably it would technically be correct but is rarely used.

Q3. $7/2 R$

P1. If the liquid water has a constant heat capacity of 4.184 J/(g) ($^{\circ}\text{C}$), 531 J/g.; from the steam tables, 532 J/g

P2. $C_p = 4.25 + 0.002 T$

P3. (a) cal/(mol)(ΔK); (b) cal/(g mol)(ΔK)(K); (c) cal/(g mol)(ΔK)(K) 2 ; (d) cal/(g mol)(ΔK)(K) 3

P4. $27,118 + 6.55T - 9.98 \times 10^{-4} T^2$

P5. 7856 J/g mol for enthalpy as ideal gas (7925 if using heat capacity equation); 5612 J/g mol for internal energy if ideal gas

P6. -1349 Btu/lb

Section 23.3

Q1. Get the enthalpy change from one table from state 1 to state 2 (the reference conditions cancel). Then get the enthalpy change from state 2 to state 3 in the second table (the reference cancel). Add the two changes.

Q2. (a) 273.16 K and 0.6113 kPa; (b) 32°F and 0.0886 psia; (c) yes

Q3. In the AE steam tables for saturated water at 250°F and 27.31 psia, the enthalpy is 218.48 Btu/lb relative to the enthalpy at 32°F and liquid at its vapor

pressure. You can neglect the enthalpy change for the change in pressure from 27.32 psia to 50 psia.

P1. 3576 Btu

P2. 3576 Btu

P3. 182 Btu

P4. -2593 kJ/kg; -2318 kJ

P5. 32.596 kJ

P6. About 262 Btu/lb

Section 23.4

Q1. Look at web sites in the supplementary references for a start.

Q2. Experiments yield raw data that is smoothed and fit by equations. Values of the properties are determined from measured values of T , p , V , and concentration plus other techniques involving special apparatus.

P1. 32,970 J

P2. 192 Btu for 2 lb using the butane chart and a heat capacity equation

P3. (a) Liquid; (b) two phase; (c) two phase; (d) vapor; (e) vapor

P4. -196 kJ/kg

P5. -393 Btu/lb (depending on the data used)

Chapter 24

Section 24.1

Q1. Both false

Q2. Yes. One example is a steady state system with $\Delta KE = \Delta PE = 0$. Then $Q + W = \Delta H$. If Q and W have the same value but opposite sign, $\Delta H = 0$.

P1. (a) $\Delta \hat{E} = 0$, $\hat{Q} = 0$, $\hat{W} \neq 0$, $\Delta \hat{PE} = 0$, $\Delta \hat{KE} = 0$; result: $\Delta \hat{H} = \hat{W}$.
(b) $\Delta \hat{E} = 0$, $\hat{Q} = 0$, $\hat{W} \neq 0$, $\Delta \hat{PE} \neq 0$, $\Delta \hat{KE} \neq 0$; result: $\Delta \hat{H} = \hat{W} - \Delta \hat{KE}$.

P2. Unsteady-state system. Assume $Q = 0$ during flow of gas. $W = 0$ (fixed cylinder walls).

$\Delta \hat{E} \neq 0$, $\Delta \hat{PE} = 0$, $\Delta \hat{KE} \neq 0$. Conclusion: $\Delta \hat{E} = \Delta \hat{U} = -\Delta \hat{H}$, or $m_2 \hat{U}_2 - m_1 \hat{U}_1 = -(m_1 - m_2) \hat{H}_{\text{flow out}}$.

P3. Steady-state system.

$\Delta \hat{E} = 0$, $\Delta \hat{PE} = 0$, $\Delta \hat{KE} = 0$, $Q \equiv 0$, hence $\Delta \hat{H} = \hat{W}$.

Section 24.2

Q1. No, but often it will.

Q2. Not if Q and W are involved, as they cannot be split among the components.

Q3. Yes

P2. 0

P3. (a) One material balance and one energy balance; (b) 0

Section 24.3

Q1. The PE of the system changes slightly because the center of mass of the system (to which the energy balance pertains) changes, and hence U changes.

P1. (a) $T = 90.1$ K; (b) $m = 1.48 \times 10^7$ g; (c) $x = 3.02 \times 10^{-4}$; (d) 49.6 hr; (e) from a handbook $T = 100$ K approximately (for a process at constant volume)

P2. (a) down; (b) probably up, depending on the room temperature; (c) down

P3. (a) $T_1 = 168.2^\circ\text{C}$, $T_2 = 99.63^\circ\text{C}$; (b) $Q = -288$ kJ/kg

P4. (a) 0; (b) 0; (c) 0; (d) if ideal gas, $\Delta T = 0$, $T_2 =$ room temperature; (e) 0.26 atm

Section 24.4

Q1. No difference except that the energy balance adds one more equation to the set used for solution and one or more unknowns.

Q2. It depends on the problem and the data provided, hence in general there is no specific choice.

Q3. Pick the reference state to be the same state as that of the stream.

Q4. If the pipe is not part of the system, then the steam enthalpy is zero in the energy balance.

P1. 8930 lb/hr using the table in Perry for benzene

P2. 99°C

P3. 1847 watts (2.48 hp)

P4. -22.5 Btu/s

Chapter 25

Section 25.1

- Q1. It is zero by definition
- Q2. It won't because by definition the standard heat of formation is at 25°C and 1 atm.
- Q3. No
- P1. $-36.4 \text{ kJ/g mol HBr}$
- P2. Assume open, steady-state system with negligible change in KE and PE , and $W = 0$.
- P3. Yes. $\Delta E = \Delta U = \Delta H - \Delta(pV)$. If $W = 0$, $\Delta KE = 0$, $\Delta PE = 0$ inside the system, and V is constant, all at 25°C and 1 atm.
- P4. $-74.83 \text{ kJ/g mol CH}_4$ compared with -74.84 in Appendix F

Section 25.2

- Q1. Yes
- Q2. No
- Q3. It should not change the value if the chemical reaction is written with the proper phases and temperatures and pressures denoted for each species.
- Q4. (a) Exothermic reaction; (b) endothermic reaction
- Q5. Yes, but it may not prove to be convenient.
- Q6. The heat of reaction is the enthalpy change at some temperature and pressure for a given number of moles; the standard heat of reaction is the enthalpy change at SC for complete reaction according to the reaction equation per unit mole of a compound.
- P1. $597.32 \text{ kJ/g mol C}_6\text{H}_6$ (benzene)
- P2. $-616 \text{ kJ/g mol C}_3\text{H}_8$ (l) using 10.18 kJ/g mol for the liquid propane from 25°C to 90°C.

Section 25.3

- Q1. In using the heat of reaction in the energy balance, the heats of formation are lumped together. When the heats of formation are merged with the enthalpies of the sensible heats and phase changes, the components of the heat of reaction are split up and no longer appear as an amalgamated term.

- Q2.** Advantages: easier to use for problems in which (1) multiple reactions occur, (2) the reaction equation(s) is unknown, (3) standard software is used. Disadvantages: (1) heats of formation of a compound are unknown and cannot be estimated, (2) only experimental data is available for the reaction enthalpy.
- P1.** -720.82 kJ (removed)
- P2.** -416.68 kJ (removed)
- P3.** -110.6 kJ (removed)

Section 25.4

- Q1.** The reference for the heats of combustion is zero for the righthand side of the chemical equation whereas the reference for the heats of formation is zero for the lefthand side of the chemical equation.
- Q2.** Yes, if none of the compounds in the chemical equation can undergo a phase transition.
- Q3.** No
- Q4.** No
- Q5.** If you pick the same basis for the heat of reaction, namely 1 gram mole of H_2 , it makes no difference. However, if you want the heat of reaction for the chemical equation as written, the calculated heat of reaction will be two times the first calculation if the original chemical equation is multiplied by two.
- Q6.** None (no water is involved)
- P1.** 234 Btu/ft^3 at 60°F and 30.0 in. Hg
- P2.** $250.2 \text{ kJ/g mol CO}$

Chapter 26

Section 26.1

- Q1.** Yes
- Q2.** A complicated problem. You should include the pressures, but you might have to assume a pressure such as 1 atm if the pressure is not specified. Sometimes you can assume two pressures are equal. Leaving them out from a degree-of-freedom analysis in effect specifies them as known.
- Q3.** No, unless you make a mistake.

- P1.** Species in: 1, species out: 5, temperatures: 2, pressures: 2, Q : 1, total 13; Equations: 3 element balances, 1 energy balance, 2 sum of components, 1 basis, 2 fraction conversions, 2 temperatures (T_{out} is implied at 450°F), 2 pressures (assumed) for a total of 13. No additional specifications needed.
- P2.** Fourteen variables and 14 equations, hence the degrees of freedom are zero; no.

Section 26.2

- Q1.** The energy balance indicates only so much energy can be associated with the output stream(s).
- Q2.** Yes
- Q3.** Yes
- P1.** If H_2O is a gas, 125 Btu/ft^3 at S. C. ($4.69 \times 10^{-3} \text{ kJ/m}^3$ at SC); if H_2O is a liquid: $5.08 \times 10^{-3} \text{ kJ/m}^3$ at SC (136 Btu/ft^3)
- P2.** 6100 Btu/lb methane absorbed by water
- P3.** 0.52 lb
- P4.** 975 K

Chapter 27

Section 27.1

- Q1.** The equation is valid only under certain assumptions: (a) no work other than work of expansion, (b) the process is reversible, (c) work is minus if done by the system.
- Q2.** If the process is a closed system in the steady state, you can: $\Delta E = 0$, $\Delta H = 0$, and $Q = -W$
- Q3.** (a) Yes; (b) yes
- Q4.** The reversible process (because it yields the maximum work) for both.
- Q5.** See text
- P1.** $W = 27.6 \text{ kJ}$; $Q = -27.6 \text{ kJ}$; $\Delta E = \Delta H = 0$
- P2.** No work is done *on* the system. Work done by the system I (a) -1370 J and (b) -1670 J ; the latter value assumes the expansion is isothermal.

Section 27.2

- Q1.** A program is possible, but cannot achieve three times the efficiency of 37% of existing cars.
- Q2.** An electric pot—the loss is just from the pot to the air. Microwave heating is the worst because electric energy must first be converted to microwave energy (88% efficiency) and then to thermal energy (43% efficiency).
- P1.** 66%
- P2.** Using data from Table 27.2: 25%
- P3.** 39.5 Btu

Section 27.3

- Q1.** (a) The process is reversible, incompressible fluid, $W = 0$; (b) pumping water, windmill, fluid flow in general.
- Q2.** They have units of length if you divide each term by g .
- Q3.** Less because real processes involve friction.
- Q4.** No. Examine the Bernoulli equation. An ideal fluid can flow from lower to higher pressure by flowing through an expanding pipe so that the velocity decreases, or by flow downhill through a pipe so that h decreases.
- Q5.** Friction causes energy loss.
- P1.** 38.8 hp
- P2.** In a pipeline the change in kinetic energy is essentially zero. The water cannot accelerate (unless the pipe diameter changes or the density changes). Water flowing downhill does not accelerate. However, a waterfall is different. Water is not affected by water before or after it in the flow, and can accelerate so that the kinetic energy change is positive.
- P3.** 9.39 m/s; there will be a significant correction for flow through an orifice.

Chapter 28**Section 28.1**

- Q1.** Look at Figure 28.2 and Section 28.1
- Q2.** (a) F; (b) F; (c) T; (d) T; (e) T
- Q3.** (a) 25°C and 1 atm; (b) 0
- Q4.** (a) Reference for HCl is 25°C and 1 atm; (b) $-92,311$ J/g mol HCl

- P1.** 2265 J per 2 g mol soln
P2. 8284 J
P3. $-865.376 \text{ J/g mol H}_2\text{SO}_4$

Section 28.2

- Q1.** Yes, usually
Q2. (a) A strong acid such as HCl in water; (b) NaCl, KCl, and others salts in water
Q3. All false
Q4. Horizontal scales differ in units. No equilibrium data. Enthalpy change not given—must be calculated
P1. -19.480 kJ/g mol (heat transfer is from the solution to the surroundings)
P2. $Q = -1.61 \times 10^6 \text{ Btu}$
P3. Two phase. For the liquid:
 $\omega_{\text{H}_2\text{O}} = 0.50$ and $\Delta\hat{H} = 8 \text{ Btu/lb}$; for the vapor $\omega_{\text{H}_2\text{O}} = 1.00$ and $\Delta\hat{H} = 1174 \text{ Btu/lb}$
P4. 500 Btu/lb

Chapter 29

Section 29.1

- Q1.** See text
Q2. Yes
Q3. Yes
Q4. The wet-bulb temperature is the temperature of the evaporating water that is in equilibrium with the ambient air that has a temperature called the dry-bulb temperature.
Q5. No
P1. (a) 3; (b) 2
P2. See Figure 29.3
P3. About $15 \text{ ft}^3/\text{lb}$ dry air
P4. 20.6 kJ/kg dry air

Section 29.2

Q1. See Section 29.2

Q2. See Section 29.2

Q3. Yes

Q4. Yes

P1. (a) 133°F; (b) the same

P2. (a) 40%; (b) 52°C

P3. (a) 0.03 kg/kg dry air; (b) 1.02 m³/kg dry air; (c) 38°C_{in}; (d) 151 kJ/kg dry air; (e) 31.5°C

P4. (a) $\mathcal{H} = 0.0808$ lb H₂O/lb dry air; (b) $H = 118.9$ Btu/lb dry air; (c) $V = 16.7$ ft³/lb dry air; (d) $\mathcal{H} = 0.0710$ lb H₂O/lb dry air

Section 29.3

Q1. Usually it is OK, but in a flue gas, for example, you want to make sure that condensation in the exit duct does not occur so that entering moisture may be important to include in the calculations.

Q2. No

P1. (a) 18 Btu/lb dry air; (b) 7×10^{-3} lb H₂O/lb dry air

P2. 49,700 Btu

P3. (a) 1.94×10^6 ft³/hr; (b) 3.00×10^4 ft³/h; (c) 2.44×10^5 Btu/hr

APPENDIX B

ATOMIC WEIGHTS AND NUMBERS

TABLE B.1 Relative Atomic Weights, 1965 (Based on the Atomic Mass of $^{12}\text{C} = 12$)

The values for atomic weights given in the table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and, further, to natural mixtures that do not include isotopes of radiogenic origin.

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	—	Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	—	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	—
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	—	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	—	Nobelium	No	102	—
Beryllium	Be	4	9.0122	Osmium	Os	75	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.4
Bromine	Br	35	79.904	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Caesium	Cs	55	132.905	Plutonium	Pu	94	—
Calcium	Ca	20	40.08	Polonium	Po	84	—
Californium	Cf	98	—	Potassium	K	19	39.102
Carbon	C	6	12.01115	Praseodym	Pr	59	140.907
Cerium	Ce	58	140.12	Promethium	Pm	61	—
Chlorine	Cl	17	35.453 ^b	Protactinium	Pa	91	—
Chromium	Cr	24	51.996 ^b	Radium	Ra	88	—
Cobalt	Co	27	58.9332	Radon	Rn	86	—
Copper	Cu	29	63.546 ^b	Rhenium	Re	75	186.2
Curium	Cm	96	—	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	84.57
Einsteinium	Es	99	—	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100	—	Selenium	Se	34	78.96
Flourine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	—	Silver	Ag	47	107.868
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	—
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	59	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lr	103	—	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	—				

SOURCE: *Comptes Rendus*, 23rd IUPAC Conference, 1965, Butterworth's, London, 1965, pp. 177–178.

APPENDIX C

TABLES OF THE PITZER Z^0 AND Z^1 FACTORS

Table C.1 Values of z^0 (from Lee, B. I., and M. G. Kessler, *AIChEJ*, 21, 510-518 (1975)).

T_r	P_r														
	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.30	0.0029	0.0145	0.0290	0.0579	0.1158	0.1737	0.2315	0.2892	0.3470	0.4335	0.5775	0.8648	1.4366	2.0048	2.8507
0.35	0.0026	0.0130	0.0261	0.0522	0.1043	0.1564	0.2084	0.2604	0.3123	0.3901	0.5195	0.7775	1.2902	1.7987	2.5539
0.40	0.0024	0.0119	0.0239	0.0477	0.0953	0.1429	0.1904	0.2379	0.2853	0.3563	0.4744	0.7095	1.1758	1.6373	2.3211
0.45	0.0022	0.0110	0.0221	0.0442	0.0882	0.1322	0.1762	0.2200	0.2638	0.3294	0.4384	0.6551	1.0841	1.5077	2.1338
0.50	0.0021	0.0103	0.0207	0.0413	0.0825	0.1236	0.1647	0.2056	0.2465	0.3077	0.4092	0.6110	1.0094	1.4017	1.9801
0.55	0.9804	0.0098	0.0195	0.0390	0.0778	0.1166	0.1553	0.1939	0.2323	0.2899	0.3853	0.5747	0.9475	1.3137	1.8520
0.60	0.9849	0.0093	0.0186	0.0371	0.0741	0.1109	0.1476	0.1842	0.2207	0.2753	0.3657	0.5446	0.8959	1.2398	1.7440
0.65	0.9881	0.9377	0.0178	0.0356	0.0710	0.1063	0.1415	0.1765	0.2113	0.2634	0.3495	0.5197	0.8526	1.773	1.6519
0.70	0.9904	0.9504	0.8958	0.0344	0.0687	0.1027	0.1366	0.1703	0.2038	0.2538	0.3364	0.4991	0.8161	1.1241	1.5729
0.75	0.9922	0.9598	0.9165	0.0336	0.0670	0.1001	0.1330	0.1656	0.1981	0.2464	0.3260	0.4823	0.7854	1.0787	1.5047
0.80	0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307	0.1626	0.1942	0.2411	0.3182	0.4690	0.7598	1.0400	1.4456
0.85	0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301	0.1614	0.1924	0.2382	0.3132	0.4591	0.7388	1.0071	1.3943
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321	0.1630	0.1935	0.2383	0.3114	0.4527	0.7220	0.9793	1.3496
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359	0.1664	0.1963	0.2405	0.3122	0.4507	0.7138	0.9648	1.3257
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	0.1410	0.1705	0.1998	0.2432	0.3138	0.4501	0.7092	0.9561	1.3108
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779	0.2055	0.2474	0.3164	0.4504	0.7052	0.9480	1.2968
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844	0.2097	0.2503	0.3182	0.4508	0.7035	0.9442	1.2901
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959	0.2154	0.2538	0.3204	0.4514	0.7018	0.9406	1.2835
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6353	0.2901	0.2237	0.2583	0.3229	0.4522	0.7004	0.9372	1.2772
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648	0.2370	0.2640	0.3260	0.4533	0.6991	0.9339	1.2710
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710	0.5146	0.2629	0.2715	0.3297	0.4547	0.6980	0.9307	1.2650
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026	0.4437	0.3131	0.3452	0.4604	0.6956	0.9222	1.2481
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880	0.5984	0.4580	0.3953	0.4770	0.6950	0.9110	1.2232
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443	0.6803	0.5798	0.4760	0.5042	0.6987	0.9033	1.2021
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858	0.7363	0.6605	0.5605	0.5425	0.7069	0.8990	1.1844

1.30	0.9985	0.9926	0.9852	0.9702	0.9396	0.9083	0.8764	0.8438	0.8111	0.7624	0.6908	0.6344	0.7358	0.8998	1.1580
1.40	0.9988	0.9942	0.9884	0.9768	0.9534	0.9298	0.9062	0.8827	0.8595	0.8256	0.7753	0.7202	0.7761	0.9112	1.1419
1.50	0.9991	0.9954	0.9909	0.9818	0.9636	0.9456	0.9278	0.9103	0.8933	0.8689	0.8328	0.7887	0.8200	0.9297	1.1339
1.60	0.9993	0.9964	0.9928	0.9856	0.9714	0.9575	0.9439	0.9308	0.9180	0.9000	0.8738	0.8410	0.8617	0.9518	1.1320
1.70	0.9994	0.9971	0.9943	0.9886	0.9775	0.9667	0.9563	0.9463	0.9367	0.9234	0.9043	0.8809	0.8984	0.9745	1.1343
1.80	0.9995	0.9977	0.9955	0.9910	0.9823	0.9739	0.9659	0.9583	0.9511	0.9413	0.9275	0.9118	0.9297	0.9961	1.1391
1.90	0.9996	0.9982	0.9964	0.9929	0.9861	0.9796	0.9735	0.9678	0.9624	0.9552	0.9456	0.9359	0.9557	1.0157	1.1452
2.00	0.9997	0.9986	0.9972	0.9944	0.9892	0.9842	0.9796	0.9754	0.9715	0.9664	0.9599	0.9550	0.9772	1.0328	1.1516
2.20	0.9998	0.9992	0.9983	0.9967	0.9937	0.9910	0.9886	0.9865	0.9847	0.9826	0.9806	0.9827	1.0094	1.0600	1.1635
2.40	0.9999	0.9996	0.9991	0.9983	0.9969	0.9957	0.9948	0.9941	0.9936	0.9935	0.9945	1.0011	1.0313	1.0793	1.1728
2.60	1.0000	0.9998	0.9997	0.9994	0.9991	0.9990	0.9990	0.9993	0.9998	1.0010	1.0040	1.0137	1.0463	1.0926	1.1792
2.80	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0021	1.0031	1.0042	1.0063	1.0106	1.0223	1.0565	1.1016	1.1830
3.00	1.0000	1.0002	1.0004	1.0008	1.0018	1.0030	1.0043	1.0057	1.0074	1.0101	1.0153	1.0284	1.0635	1.1075	1.1848
3.50	1.0001	1.0004	1.0008	1.0017	1.0035	1.0055	1.0075	1.0097	1.0120	1.0156	1.0221	1.0368	1.0723	1.1138	1.1834
4.00	1.0001	1.0005	1.0010	1.0021	1.0043	1.0066	1.0090	1.0115	1.0140	1.0179	1.0249	1.0401	1.0747	1.1136	1.1773

The shaded region contains values for the liquid phase.

Table C.2 Values of z^1 (from Lee, B. I. and M. G. Kessler, *AIChEJ*, 21, 510-518 (1975)).

T_r	P_r														
	0.10	0.50	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.30	-0.0008	-0.0040	-0.0081	-0.0161	-0.0323	-0.0484	-0.0645	-0.0806	-0.0966	-0.1207	-0.1608	-0.2407	-0.3996	-0.5572	-0.7915
0.35	-0.0009	-0.0046	-0.0093	-0.0185	-0.0370	-0.0554	-0.0738	-0.0921	-0.1105	-0.1379	-0.1834	-0.2738	-0.4523	-0.6279	-0.8863
0.40	-0.0010	-0.0048	-0.0095	-0.0190	-0.0380	-0.0570	-0.0758	-0.0946	-0.1134	-0.1414	-0.1879	-0.2799	-0.4603	-0.6365	-0.8936
0.45	-0.0009	-0.0047	-0.0094	-0.0187	-0.0374	-0.0560	-0.0745	-0.0929	-0.1113	-0.1387	-0.1840	-0.2734	-0.4475	-0.6162	-0.8606
0.50	-0.0009	-0.0045	-0.0090	-0.0181	-0.0360	-0.0539	-0.0716	-0.0893	-0.1069	-0.1330	-0.1762	-0.2611	-0.4253	-0.5831	-0.8099
0.55	-0.0314	-0.0043	-0.0086	-0.0172	-0.0343	-0.0513	-0.0682	-0.0849	-0.1015	-0.1263	-0.1669	-0.2465	-0.3991	-0.5446	-0.7521
0.60	-0.0205	-0.0041	-0.0082	-0.0164	-0.0326	-0.0487	-0.0646	-0.0803	-0.0960	-0.1192	-0.1572	-0.2312	-0.3718	-0.5047	-0.6928
0.65	-0.0137	-0.0772	-0.0078	-0.0156	-0.0309	-0.0461	-0.0611	-0.0759	-0.0906	-0.1122	-0.1476	-0.2160	-0.3447	-0.4653	-0.6346
0.70	-0.0093	-0.0507	-0.1161	-0.0148	-0.0294	-0.0438	-0.0579	-0.0718	-0.0855	-0.1057	-0.1385	-0.2013	-0.3184	-0.4270	-0.5785
0.75	-0.0064	-0.0339	-0.0744	-0.0143	-0.0282	-0.0417	-0.0550	-0.0681	-0.0808	-0.0996	-0.1298	-0.1872	-0.2929	-0.3901	-0.5250
0.80	-0.0044	-0.0228	-0.0487	-0.1160	-0.0272	-0.0401	-0.0526	-0.0648	-0.0767	-0.0940	-0.1217	-0.1736	-0.2682	-0.3545	-0.4740
0.85	-0.0029	-0.0152	-0.0319	-0.0715	-0.0268	-0.0391	-0.0509	-0.0622	-0.0731	-0.0888	-0.1138	-0.1602	-0.2439	-0.3201	-0.4254
0.90	-0.0019	-0.0099	-0.0205	-0.0442	-0.1118	-0.0396	-0.0503	-0.0604	-0.0701	-0.0840	-0.1059	-0.1463	-0.2195	-0.2862	-0.3788
0.93	-0.0015	-0.0075	-0.0154	-0.0326	-0.0763	-0.1662	-0.0514	-0.0602	-0.0687	-0.0810	-0.1007	-0.1374	-0.2045	-0.2661	-0.3516
0.95	-0.0012	-0.0062	-0.0126	-0.0262	-0.0389	-0.1110	-0.0340	-0.0607	-0.0678	-0.0788	-0.0967	-0.1310	-0.1943	-0.2526	-0.3339
0.97	-0.0010	-0.0050	-0.0101	-0.0208	-0.0450	-0.0770	-0.1647	-0.0623	-0.0669	-0.0759	-0.0921	-0.1240	-0.1837	-0.2391	-0.3163
0.98	-0.0009	-0.0044	-0.0090	-0.0184	-0.0390	-0.0641	-0.1100	-0.0641	-0.0661	-0.0740	-0.0893	-0.1202	-0.1783	-0.2322	-0.3075
0.99	-0.0008	-0.0039	-0.0079	-0.0161	-0.0335	-0.0531	-0.0796	-0.0680	-0.0646	-0.0715	-0.0861	-0.1162	-0.1728	-0.2254	-0.2989
1.00	-0.0007	-0.0034	-0.0069	-0.0140	-0.0285	-0.0435	-0.0588	-0.0879	-0.0609	-0.0678	-0.0824	-0.1118	-0.1672	-0.2185	-0.2902
1.01	-0.0006	-0.0030	-0.0060	-0.0120	-0.0240	-0.0351	-0.0429	-0.0223	-0.0473	-0.0621	-0.0778	-0.1072	-0.1615	-0.2116	-0.2816
1.02	-0.0005	-0.0026	-0.0051	-0.0102	-0.0198	-0.0277	-0.0303	-0.0062	0.0227	-0.0524	-0.0722	-0.1021	-0.1556	-0.2047	-0.2731
1.05	-0.0003	-0.0015	-0.0029	-0.0054	-0.0092	-0.0097	-0.0032	0.0220	0.1059	0.0451	-0.0432	-0.0838	-0.1370	-0.1835	-0.2476
1.10	-0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236	0.0476	0.0897	0.1630	0.0698	-0.0373	-0.1021	-0.1469	-0.2056
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396	0.0625	0.0943	0.1548	0.1667	0.0332	-0.0611	-0.1084	-0.1642
1.20	0.0004	0.0019	0.0039	0.0084	0.0190	0.0326	0.0499	0.0719	0.0991	0.1477	0.1990	0.1095	-0.0141	-0.0678	-0.1231

1.30	0.0006	0.0030	0.0061	0.0125	0.0267	0.0429	0.0612	0.0819	0.1048	0.1420	0.1991	0.2079	0.0875	0.0176	-0.0423
1.40	0.0007	0.0036	0.0072	0.0147	0.0306	0.0477	0.0661	0.0857	0.1063	0.1383	0.1894	0.2397	0.1737	0.1008	0.0350
1.50	0.0008	0.0039	0.0078	0.0158	0.0323	0.0497	0.0677	0.0864	0.1055	0.1345	0.1806	0.2433	0.2309	0.1717	0.1058
1.60	0.0008	0.0040	0.0080	0.0162	0.0330	0.0501	0.0677	0.0855	0.1035	0.1303	0.1729	0.2381	0.2631	0.2255	0.1673
1.70	0.0008	0.0040	0.0081	0.0163	0.0329	0.0497	0.0667	0.0838	0.1008	0.1259	0.1658	0.2305	0.2788	0.2628	0.2179
1.80	0.0008	0.0040	0.0081	0.0162	0.0325	0.0488	0.0652	0.0816	0.0978	0.1216	0.1593	0.2224	0.2846	0.2871	0.2576
1.90	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635	0.0792	0.0947	0.1173	0.1532	0.2144	0.2848	0.3017	0.2876
2.00	0.0008	0.0039	0.0078	0.0155	0.0310	0.0464	0.0617	0.0767	0.0916	0.1133	0.1476	0.2069	0.2819	0.3097	0.3096
2.20	0.0007	0.0037	0.0074	0.0147	0.0293	0.0437	0.0579	0.0719	0.0857	0.1057	0.1374	0.1932	0.2720	0.3135	0.3355
2.40	0.0007	0.0035	0.0070	0.0139	0.0276	0.0411	0.0544	0.0675	0.0803	0.0989	0.1285	0.1812	0.2602	0.3089	0.3459
2.60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512	0.0634	0.0754	0.0929	0.1207	0.1706	0.2484	0.3009	0.3475
2.80	0.0006	0.0031	0.0062	0.0124	0.0245	0.0365	0.0483	0.0598	0.0711	0.0876	0.1138	0.1613	0.2372	0.2915	0.3443
3.00	0.0006	0.0029	0.0059	0.0117	0.0232	0.0345	0.0456	0.0565	0.0672	0.0828	0.1076	0.1529	0.2268	0.2817	0.3385
3.50	0.0005	0.0026	0.0052	0.0103	0.0204	0.0303	0.0401	0.0497	0.0591	0.0728	0.0949	0.1356	0.2042	0.2584	0.3194
4.00	0.0005	0.0023	0.0046	0.0091	0.0182	0.0270	0.0357	0.0443	0.0527	0.0651	0.0849	0.1219	0.1857	0.2379	0.2994

The shaded region contains values for the liquid phase.

APPENDIX D

PHYSICAL PROPERTIES OF VARIOUS ORGANIC AND INORGANIC SUBSTANCES

General Sources of Data for Tables on the Physical Properties, Heat Capacities, and Thermodynamic Properties in Appendices D, E, and F

1. Kobe, Kenneth A., and Associates. "Thermochemistry of Petrochemicals." Reprint from *Petroleum Refiner*, Houston: Gulf Publishing (January 1949–July 1958). (Enthalpy tables D.2–D.7 and heat capacities of several gases in Table E.1, Appendix E.)
2. Lange, N. A. *Handbook of Chemistry*, 12th ed. New York: McGraw-Hill (1979).
3. Maxwell, J. B. *Data Book on Hydrocarbons*. New York: Van Nostrand Reinhold (1950).
4. Perry, J. H., and C. H. Chilton, eds. *Chemical Engineers' Handbook*, 5th ed. New York: McGraw-Hill (1973).
5. Rossini, Frederick D., et al. "Selected Values of Chemical Thermodynamic Properties." From *National Bureau of Standards Circular 500*. Washington, DC: U.S. Government Printing Office (1952).
6. Rossini, Frederick D., et al. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds." American Petroleum Institute Research Project 44 (1953 and subsequent years).
7. Weast, Robert C. *Handbook of Chemistry and Physics*, 59th ed. Boca Raton, FL: CRC Press (1979).

TABLE D.1 Physical Properties of Various Organic and Inorganic Substances* (additional compounds are on the disk in the back of this book, provided by Professor Carl L. Yaws)

To convert to kcal/g mol, multiply by 0.2390; to Btu/lb mol multiply by 430.2.

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	$\Delta \hat{H}$ Fusion (kJ/g mol)	$\Delta \hat{H}$ Vap. at b.p. (kJ/g mol)	Normal b.p. (K)	T_c (K)	p_c (atm)	\hat{V}_c (cm ³ /g mol)	z_c
Acetaldehyde	C ₂ H ₄ O	44.05	0.783 ^{18°/4°}	149.5			293.2	461.0			
Acetic acid	CH ₃ CHO ₂	60.05	1.049	289.9	12.09	24.4	390.4	594.8	57.1	171	0.200
Acetone	C ₃ H ₆ O	58.08	0.791	178.2	5.69	30.2	329.2	508.0	47.0	213	0.238
Acetylene	C ₂ H ₂	26.04	0.9061(A)	191.7	3.7	17.5	191.7	309.5	61.6	113	0.274
Air			1.00					132.5	37.2		
Ammonia	NH ₃	17.03	0.817-79°	195.40	5.653	23.35	239.73	405.5	111.3	72.5	0.243
Ammonium carbonate	(NH ₄) ₂ CO ₃ ·H ₂ O	114.11	0.597(A)								
Ammonium chloride	NH ₄ Cl	53.50	2.53 ^{17°}								
Ammonium nitrate	NH ₄ NO ₃	80.05	1.725 ^{25°}	442.8	5.4				(decomposes at 483.2 K)		
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.14	1.769	786					(decomposes at 786 K after melting)		
Aniline	C ₆ H ₇ N	93.12	1.022	266.9			457.4	699	52.4		
Benzaldehyde	C ₆ H ₅ CHO	106.12	1.046	247.16			452.16	38.40			
Benzene	C ₆ H ₆	78.11	0.879	278.693	9.837	30.76	353.26	562.6	48.6	260	0.274
Benzoic acid	C ₇ H ₆ O ₂	122.12	1.316 ^{28°/4°}	395.4			523.0				
Benzyl alcohol	C ₇ H ₈ O	108.13	1.045	257.8			478.4				
Boron oxide	B ₂ O ₃	69.64	1.85	723	22.0						
Bromine	Br ₂	159.83	3.119 ^{20°}	265.8	10.8	31.0	331.78	584	102	144	0.306
1, 2-Butadiene	C ₄ H ₆	54.09	5.87(A)								
1, 3-Butadiene	C ₄ H ₆	54.09	0.652 ^{20°}	136.7			283.3	446			
Butane	n-C ₄ H ₁₀	58.12	0.621	164.1			268.6	425	42.7	221	0.271
iso-Butane	iso-C ₄ H ₁₀	58.12	0.579	134.83	4.661	22.31	272.66	425.17	37.47	255	0.374
			0.557	113.56	4.540	21.29	261.43	408.1	36.0	263	0.283

*Sources of data are listed at the beginning of Appendix D.
Sp gr = 20°C/4°C unless specified. Sp gr for gas referred to air (A).

TABLE D.1 (cont.)

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	$\Delta \hat{H}$ Fusion (kJ/g mol)	Normal b.p. (K)	$\Delta \hat{H}$ Vap. at b.p. (kJ/g mol)	T_c (K)	p_c (atm)	\hat{V}_c (cm ³ /g mol)	z_c
1-Butene	C ₄ H ₈	56.10	0.60	87.81	3.848	266.91	21.92	419.6	39.7	240	0.277
Butyl phthalate	<i>see</i> Dibutyl phthalate										
<i>n</i> -Butyric acid	<i>n</i> -C ₄ H ₈ O ₂	88.10	0.958	267		437.1		628	52.0	290	0.293
iso-Butyric acid	iso-C ₄ H ₈ O ₂	88.10	0.949	226		427.7		609			
Calcium arsenate	Ca ₃ (AsO ₄) ₂	398.06		1723							
Calcium carbide	Ca ₂ C ₂	64.10	2.2218°	2573							
Calcium carbonate	CaCO ₃	100.09	2.93	(decomposes at 1098 K)							
Calcium chloride	CaCl ₂	110.99	2.15215°	1055	28.4						
	CaCl ₂ ·H ₂ O	129.01									
	CaCl ₂ ·2H ₂ O	147.03									
	CaCl ₂ ·6H ₂ O	219.09	1.7817°	303.4	37.3	(-6H ₂ O at 473 K)					
Calcium cyanamide	CaCN ₂	80.11	2.29								
Calcium cyanide	Ca(CN) ₂	92.12									
Calcium hydroxide	Ca(OH) ₂	74.10	2.24	(-H ₂ O at 853 K)							
Calcium oxide	CaO	56.08	2.62	2873	50	3123					
Calcium phosphate	Ca ₃ (PO ₄) ₂	310.19	3.14	1943							
Calcium silicate	CaSiO ₃	117.17	2.915	1803	48.62						
Calcium sulfate (gypsum)	CaSO ₄ ·2H ₂ O	172.18	2.32	(-1½ H ₂ O at 301° K)							
Carbon	C	12.010	2.26	3873	46.0	4473					
Carbon dioxide	CO ₂	44.01	1.53(A)	217.05.2atm	8.32	(sublimes at 195 K)		304.2	72.9	94	0.275
			1.229 satd. liq. at 5162 kPa								

Carbon disulfide	CS ₂	76.14	1.261 ^{22°/20°} 2.63(A)	161.1	4.39	319.41	26.8	552.0	78.0	170	0.293
Carbon monoxide	CO	28.01	0.968(A)	68.10	0.837	81.66	6.042	133.0	34.5	93	0.294
Carbon tetrachloride	CCl ₄	153.84	1.595	250.3	2.5	349.9	30.0	556.4	45.0	276	0.272
Chlorine	Cl ₂	70.91	2.49(A)	172.16	6.406	239.10	20.41	417.0	76.1	124	0.276
Chlorobenzene	C ₆ H ₅ Cl	112.56	1.107	228		405.26	36.5	632.4	44.6	308	0.265
Chloroform	CHCl ₃	119.39	1.489 ^{20°}	209.5		334.2		536.0	54.0	240	0.294
Chromium	Cr	52.01	7.1								
Copper	Cu	63.54	8.92	1356.2	13.0	2855	305				
Cumene	C ₉ H ₁₂	120.19	0.862	177.125	7.1	425.56	37.5	636	31.0	440	0.260
Cupric sulfate	CuSO ₄	159.61	3.605 ^{15°}	(decomposes at 873 K)							
Cyclohexane	C ₆ H ₁₂	84.16	0.779	279.83	2.677	353.90	30.1	553.7	40.4	308	0.274
Cyclopentane	C ₅ H ₁₀	70.13	0.745	179.71	0.6088	322.42	27.30	511.8	44.55	260	0.27
Decane	C ₁₀ H ₂₂	142.28	0.730 ^{20°}	243.3		447.0		619.0	20.8	602	0.2476
Dibutyl phthalate	C ₈ H ₂₂ O ₄	278.34	1.045 ^{21°}			613					
Diethyl ether	(C ₂ H ₅) ₂ O	74.12	0.708 ^{25°}	156.86	7.301	307.76	26.05	467	35.6	281	0.261
Ethane	C ₂ H ₆	30.07	1.049(A)	89.89	2.860	184.53	14.72	305.4	48.2	148	0.285
Ethanol	C ₂ H ₆ O	46.07	0.789	158.6	5.021	351.7	38.6	516.3	63.0	167	0.248
Ethyl acetate	C ₄ H ₈ O ₂	88.10	0.901	189.4		350.2		523.1	37.8	286	0.252
Ethyl benzene	C ₈ H ₁₀	106.16	0.867	178.185	9.163	409.35	36.0	619.7	37.0	360	0.260
Ethyl bromide	C ₂ H ₅ Br	108.98	1.460	154.1		311.4		504	61.5	215	0.320
Ethyl chloride	CH ₃ CH ₂ Cl	64.52	0.903 ^{10°}	134.83	4.452	285.43	25	460.4	52.0	199	0.274
3-Ethyl hexane	C ₈ H ₁₈	114.22	0.7169			391.69	34.3	567.0	26.4	466	0.264
Ethylene	C ₂ H ₄	28.05	0.975(A)	103.97	3.351	169.45	13.54	283.1	50.5	124	0.270
Ethylene glycol	C ₂ H ₆ O ₂	62.07	1.113 ^{19°}	260	11.23	470.4	56.9				
Ferric oxide	Fe ₂ O ₃	159.70	5.12	1833		(decomposes at 1833 K)					
Ferric sulfide	Fe ₂ S ₃	207.90	4.3	(decomposes)							

*Sources of data are listed at the beginning of Appendix D.


Sp gr = 20°C/4°C unless specified. Sp gr for gas referred to air (A).

TABLE D.1 (cont.)

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	ΔH Fusion (kJ/g mol)	Normal b.p. (K)	ΔH Vap. at b.p. (kJ/g mol)	T_c (K)	p_c (atm)	\hat{V}_c (cm ³ /g mol)	z_c
Ferrous sulfide	FeS	87.92	4.84	1466	(decomposes)						
Formaldehyde	H ₂ CO	30.03	0.815 ^{-20°}	154.9		253.9	24.5				
Formic acid	CH ₂ O ₂	46.03	1.220	281.46	12.7	373.7	22.3				
Glycerol	C ₃ H ₈ O ₃	92.09	1.260 ^{50°}	291.36	18.30	563.2					
Helium	He	4.00	0.1368(A)	3.5	0.02	4.216	0.084	5.26	2.26	58	0.304
Heptane	C ₇ H ₁₆	100.20	0.684	182.57	14.03	371.59	31.69	540.2	27.0	426	0.260
Hexane	C ₆ H ₁₄	86.17	0.659	177.84	13.03	341.90	28.85	507.9	29.9	368	0.264
Hydrogen	H ₂	2.016	0.06948(A)	13.96	0.12	20.39	0.904	33.3	12.8	65	0.304
Hydrogen chloride	HCl	36.47	1.268(A)	158.94	1.99	188.11	16.15	324.6	81.5	87	0.266
Hydrogen fluoride	HF	20.01	1.15	238		293		503.2			
Hydrogen sulfide	H ₂ S	34.08	1.1895(A)	187.63	2.38	212.82	18.67	373.6	88.9	98	0.284
Iodine	I ₂	253.8	4.93 ^{20°}	386.5		457.4		826.0			
Iron	Fe	55.85	7.7	1808	15	3073	353				
Iron oxide	Fe ₃ O ₄	231.55	5.2	1867	138	(decomposes at 1867 K after melting)					
Lead	Pb	207.21	11.337 ^{20°}	600.6	5.10	2023	180				
Lead oxide	PbO	223.21	9.5	1159	11.7	1745	213				
Magnesium	Mg	24.32	1.74	923	9.2	1393	132				
Magnesium chloride	MgCl ₂	95.23	2.325 ^{25°}	987	43.1	1691	137				
Magnesium hydroxide	Mg(OH) ₂	58.34	2.4	(decomposes at 623 K)							
Magnesium oxide	MgO	40.32	3.65	3173	77.4	3873					
Mercury	Hg	200.61	13.546 ^{20°}								
Methane	CH ₄	16.04	0.554(A)	90.68	0.941	111.67	8.180	190.7	45.8	99	0.290
Methanol	CH ₃ OH	32.04	0.792	175.26	3.17	337.9	35.3	513.2	78.5	118	0.222
Methyl acetate	C ₃ H ₆ O ₂	74.08	0.933	174.3		330.3		506.7	46.3	228	0.254

TABLE D.1 (cont.)

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	$\Delta \hat{H}_f$ Fusion (kJ/g mol)	Normal b.p. (K)	$\Delta \hat{H}_v$ at b.p. (kJ/g mol)	T_c (K)	p_c (atm)	\hat{V}_c (cm ³ /g mol)	z_c
Phenyl hydrazine	C ₆ H ₈ N ₂	108.14	1.097 ^{23°}	292.76	16.43	51.66					
Phosphoric acid	H ₃ PO ₄	98.00	1.834 ^{18°}	315.51	10.5	(-½ H ₂ O at 486 K)					
Phosphorus (red)	P ₄	123.90	2.20	863	81.17	863	41.84				
Phosphorus (white)	P ₄	123.90	1.82	317.4	2.5	553	49.71				
Phosphorus pentoxide	P ₂ O ₅	141.95	2.387	(sublimes at 523 K)							
Propane	C ₃ H ₈	44.09	1.562(A)	85.47	3.524	231.09	18.77	369.9	42.0	200	0.277
Propene	C ₃ H ₆	42.08	1.498(A)	87.91	3.002	255.46	18.42	365.1	45.4	181	0.274
Propionic acid	C ₃ H ₆ O ₂	74.08	0.993	252.2		414.4		612.5	53.0		
n-Propyl alcohol	C ₃ H ₈ O	60.09	0.804	146		370.2		536.7	49.95	220	0.251
iso-Propyl alcohol	C ₃ H ₈ O	60.09	0.785	183.5		355.4		508.8	53.0	219	0.278
n-Propyl benzene	C ₉ H ₁₂	120.19	0.862	173.660	8.54	432.38	38.2	638.7	31.3	429	0.257
Silicon dioxide	SiO ₂	60.09	2.25	1883	8.54	2503					
Sodium bisulfate	NaHSO ₄	120.07	2.742	455							
Sodium carbonate (sal soda)	Na ₂ CO ₃ ·10H ₂ O	286.15	1.46	306.5		(-H ₂ O at 306.5 K)					
Sodium carbonate (soda ash)	Na ₂ CO ₃	105.99	2.533	1127	33.4	(decomposes)					
Sodium chloride	NaCl	58.45	2.163	1081	28.5	1738	171				
Sodium cyanide	NaCN	49.01		835	16.7	1770	155				
Sodium hydroxide	NaOH	40.00	2.130	592	8.4	1663					
Sodium nitrate	NaNO ₃	85.00	2.257	583	15.9	(decomposes at 653 K)					
Sodium nitrite	NaNO ₂	69.00	2.168 ^{0°}	544		(decomposes at 593 K)					
Sodium sulfate	Na ₂ SO ₄	142.05	2.698	1163	24.3						
Sodium sulfide	Na ₂ S	78.05	1.856	1223	6.7						
Sodium sulfite	Na ₂ SO ₃	126.05	2.633 ^{15°}	(decomposes)							

Sodium thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3$	158.11	1.667						
Sulfur (rhombic)	S_8	256.53	2.07	386	10.0	717.76	84		
Sulfur (monoclinic)	S_8 	256.53	1.96	392	14.17	717.76	84		
Sulfur chloride (mono)	S_2Cl_2	135.05	1.687	193.0		411.2	36.0		
Sulfur dioxide	SO_2	64.07	2.264(A)	197.68	7.402	263.14	24.92	430.7	77.8 122
Sulfur trioxide	SO_3	80.07	2.75(A)	290.0	24.5	316.5	41.8	491.4	83.8 126
Sulfuric acid	H_2SO_4	98.08	1.834 ^{18°}	283.51	9.87			(decomposes at 613 K)	
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	92.13	0.866	178.169	6.619	383.78	33.5	593.9	40.3 318
Water	H_2O	18.016	1.004°	273.16	6.009	373.16	40.65	647.4	218.3 56
<i>m</i> -Xylene	C_8H_{10}	106.16	0.864	225.288	11.57	412.26	34.4	619	34.6 390
<i>o</i> -Xylene	C_8H_{10}	106.16	0.880	247.978	13.60	417.58	36.8	631.5	35.7 380
<i>p</i> -Xylene	C_8H_{10}	106.16	0.861	286.423	17.11	411.51	36.1	618	33.9 370
Zinc	Zn	65.38	7.140	692.7	6.673	1180	114.8		
Zinc sulfate	ZnSO_4	161.44	3.74 ^{15°}	(decomposes at 1013 K)					

*Sources of data are listed at the beginning of Appendix D.
 Sp gr = 20°C/4°C unless specified. Sp gr for gas referred to air (A).

TABLE D.2 Enthalpies of Paraffinic Hydrocarbon Vapors, C_1 – C_6 (J/g mol) (at 1 atm)

To convert to Btu/lb mol, multiply by 0.4306.

K	C_1	C_2	C_3	n - C_4	i - C_4	n - C_5	n - C_6
273	0						
291	630	912	1,264	1,709	1,658	2,125	2,545
298	879	1,277	1,771	2,394	2,328	2,976	3,563
300	950	1,383	1,919	2,592	2,522	3,222	3,858
400	4,740	7,305	10,292	13,773	13,623	17,108	20,463
500	9,100	14,476	20,685	27,442	27,325	34,020	40,622
600	14,054	22,869	32,777	43,362	43,312	53,638	64,011
700	19,585	32,342	46,417	61,186	61,220	75,604	90,123
800	25,652	42,718	61,337	80,600	80,767	99,495	118,532
900	32,204	53,931	77,404	101,378	101,754	125,101	148,866
1,000	39,204	65,814	94,432	123,428	123,971	152,213	181,041
1,100	46,567	78,408	112,340	146,607	147,234	180,665	214,764
1,200	54,308	91,504	131,042	170,707	171,418	210,246	249,868
1,300	62,383	105,143	150,331	195,727	196,480	240,872	286,143
1,400	70,709	119,202	170,205	221,375	222,212	272,378	323,465
1,500	79,244	133,678	190,581	247,650	248,571	304,595	361,539
1,600	88,031						
1,800	106,064						
2,000	124,725						
2,200	143,804						
2,500	173,050						

TABLE D.3 Enthalpies of Other Hydrocarbon Vapors (J/g mol) (at 1 atm)

To convert to Btu/lb mol, multiply by 0.4306.

K	Ethylene	Propylene	i -Butene	iso-Butene	Acetylene	Benzene
273	0	0	0	0	0	0
291	753	1,104	1,536	1,538	769	1,381
298	1,054	1,548	2,154	2,154	1,075	1,945
300	1,125	1,665	2,313	2,322	1,163	2,109
400	6,008	8,882	12,455	12,367	5,899	11,878
500	11,890	17,572	24,765	24,468	11,125	24,372
600	18,648	27,719	38,911	38,425	16,711	39,150
700	26,158	39,049	54,643	53,889	22,556	55,840
800	34,329	51,379	71,755	70,793	28,686	74,015
900	43,053	64,642	89,997	88,826	35,074	93,471
1,000	52,258	78,742	109,286	107,947	41,635	113,972
1,100	61,923	93,470	129,494	123,846	48,388	135,394
1,200	71,964	108,825	150,456	148,866	55,271	157,611
1,300	82,341	124,683	172,087	170,414	62,342	180,456
1,400	92,968	141,000	194,304	188,363	69,622	203,844
1,500	103,888	157,736	217,065	215,183	76,944	227,777

TABLE D.4 Enthalpies of Nitrogen and Some of its Oxides (J/g mol) (at 1 atm)
To convert to Btu/lb mol, multiply by 0.4306.

K	N ₂	NO	N ₂ O	NO ₂	N ₂ O ₄
273	0	0	0	0	0
291	524	537	686	658	1,384
298	728	746	957	917	1,937
300	786	686	1,034	985	2,083
400	3,695	3,785	5,121	4,865	10,543
500	6,644	6,811	9,582	9,070	19,915
600	9,627	9,895	14,386	13,564	30,124
700	12,652	13,054	19,513	18,305	
800	15,756	16,292	24,950	23,242	
900	18,961	19,597	30,693	28,334	
1,000	22,171	22,970	36,748	33,551	
1,100	25,472	26,392	43,129	38,869	
1,200	28,819	29,861	49,862	44,266	
1,300	32,216	33,371		49,731	
1,400	35,639	36,915		55,258	
1,500	39,145	40,488		60,826	
1,750	47,940	49,505			
2,000	56,902	58,634			
2,250	65,981	67,856			
2,500	75,060	77,127			

TABLE D.5 Enthalpies of Sulfur Compound Vapors (J/g mol) (at 1 atm)
To convert to Btu/lb mol, multiply by 0.4306.

K	S ₂ (g)	SO ₂	SO ₃	H ₂ S	CS ₂
273	0	0	0	0	0
291	579	706	899	607	807
298	805	984	1,255	845	1,125
300	869	1,064	1,338	909	1,217
400	4,196	5,234	6,861	4,372	5,995
500	7,652	9,744	13,033	7,978	11,108
600	11,192	14,514	19,832	11,752	16,455
700	14,790	19,501	27,154	15,706	21,974
800	18,426	24,647	34,748	19,840	27,631
900	22,087	29,915	42,676	24,145	33,388
1,000	25,769	35,275	50,835	28,610	39,220
1,100	29,463	40,706	59,203	33,216	45,103
1,200	33,174	46,191	67,738	37,953	51,044
1,300	36,898	51,714	76,399	42,802	57,027
1,400	40,630	57,320		47,739	63,052
1,500	44,371	62,927		52,802	69,119
1,600	48,116	68,533		57,906	75,186
1,700	51,881	74,182		63,094	81,295
1,800	55,605	79,872		68,324	87,361
1,900	59,370	85,520			
2,000	63,136	91,253			
2,500	82,006	119,871			
3,000	100,959	148,657			

TABLE D.6 Enthalpies of Combustion Gases* (J/g mol)[†]

K	N ₂	O ₂	Air	H ₂	CO	CO ₂	H ₂ O
273	0	0	0	0	0	0	0
291	524	527	523	516	525	655	603
298	728	732	726	718	728	912	837
300	786	790	784	763	786	986	905
400	3,695	3,752	3,696	3,655	3,699	4,903	4,284
500	6,644	6,811	6,660	6,589	6,652	9,204	7,752
600	9,627	9,970	9,673	9,518	9,665	13,807	11,326
700	12,652	13,225	12,736	12,459	12,748	18,656	15,016
800	15,756	16,564	15,878	15,413	15,899	23,710	18,823
900	18,961	19,970	19,116	18,384	19,125	28,936	22,760
1,000	22,171	23,434	22,367	21,388	22,413	34,308	26,823
1,100	25,472	26,940	25,698	24,426	25,760	39,802	31,011
1,200	28,819	30,492	29,078	27,509	29,154	45,404	35,312
1,300	32,216	34,078	32,501	30,626	32,593	51,090	39,722
1,400	35,639	37,693	35,953	33,789	36,070	56,860	44,237
1,500	39,145	41,337	39,463	36,994	39,576	62,676	48,848
1,750	47,940	50,555	48,325	45,275	48,459	77,445	60,751
2,000	56,902	59,914	57,320	53,680	57,488	92,466	73,136
2,250	65,981	69,454	66,441	62,341	66,567	107,738	85,855
2,500	75,060	79,119	75,646	71,211	75,772	123,176	98,867
2,750	84,265	88,910	84,935	80,290	85,018	138,699	112,089
3,000	93,512	98,826	94,265	89,453	94,265	154,347	125,520
3,500	112,131	119,034	113,135	108,030	112,968	185,895	152,799
4,000	130,875	141,410	132,172	127,528	131,796	217,777	180,414

[†]To convert to cal/g mol, multiply by 0.2390.

*Pressure = 1 atm.

SOURCE: Page 30 of Reference in Table D.7.

TABLE D.7 Enthalpies of Combustion Gases* (Btu/lb mol)

°R	N ₂	O ₂	Air	H ₂	CO	CO ₂	H ₂ O
492	0.0	0.0	0.0	0.0	0.0	0.0	0.0
500	55.67	55.93	55.57	57.74	55.68	68.95	64.02
520	194.9	195.9	194.6	191.9	194.9	243.1	224.2
537	313.2	315.1	312.7	308.9	313.3	392.2	360.5
600	751.9	758.8	751.2	744.4	752.4	963	867.5
700	1,450	1,471	1,450	1,433	1,451	1,914	1,679
800	2,150	2,194	2,153	2,122	2,154	2,915	2,501
900	2,852	2,931	2,861	2,825	2,863	3,961	3,336
1,000	3,565	3,680	3,579	3,511	3,580	5,046	4,184
1,100	4,285	4,443	4,306	4,210	4,304	6,167	5,047
1,200	5,005	5,219	5,035	4,917	5,038	7,320	5,925
1,300	5,741	6,007	5,780	5,630	5,783	8,502	6,819
1,400	6,495	6,804	6,540	6,369	6,536	9,710	7,730
1,500	7,231	7,612	7,289	7,069	7,299	10,942	8,657
1,600	8,004	8,427	8,068	7,789	8,072	12,200	9,602
1,700	8,774	9,251	8,847	8,499	8,853	13,470	10,562
1,800	9,539	10,081	9,623	9,219	9,643	14,760	11,540
1,900	10,335	10,918	10,425	9,942	10,440	16,070	12,530
2,000	11,127	11,760	11,224	10,689	11,243	17,390	13,550
2,100	11,927	12,610	12,030	11,615	12,050	18,730	14,570
2,200	12,730	13,460	12,840	12,160	12,870	20,070	15,610
2,300	13,540	14,320	13,660	12,890	13,690	21,430	16,660
2,400	14,350	15,180	14,480	13,650	14,520	22,800	17,730
2,500	15,170	16,040	15,300	14,400	15,350	24,180	18,810

*Pressure = 1 atm.

SOURCE: Page 30 Kobe, K.A., et al. *Thermochemistry of Petrochemicals*, Reprint No. 44 from the *Petroleum Refiner*, Gulf Publishing Houston, TX (1958).

APPENDIX E

HEAT CAPACITY EQUATIONS

TABLE E.1 Heat Capacity Equations for Organic and Inorganic Compounds (at Low Pressures)*

Forms: (1) $C_p^\circ = a + b(T) + c(T)^2 + d(T)^3$;

(2) $C_p^\circ = a + b(T) + c(T)^{-2}$.

Units of C_p° are J/(g mol)(K or °C).

To convert to cal/(g mol)(K or °C) = Btu/(lb mol)(°R or °F), multiply by 0.2390.

Note: $b \cdot 10^2$ means the value of b is to be multiplied by 10^{-2} , e.g., 20.10×10^{-2} for acetone.

Compound	Formula	Mol. Wt.	State	Form	T	a	$b \cdot 10^2$	$c \cdot 10^5$	$d \cdot 10^9$	Temp. Range (in °)
Acetone	CH ₃ COCH ₃	58.08	g	1	°C	71.96	20.10	-12.78	34.76	0-1200
Acetylene	C ₂ H ₂	26.04	g	1	°C	42.43	6.053	-5.033	18.20	0-1200
Air		29.0	g	1	°C	28.94	0.4147	0.3191	-1.965	0-1500
Ammonia	NH ₃	17.03	g	1	K	28.09	0.1965	0.4799	-1.965	273-1800
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.15	c	1	°C	35.15	2.954	0.4421	-6.686	0-1200
Benzene	C ₆ H ₆	78.11	l	1	K	215.9				275-328
					K	-7.27329	77.054	-164.82	1,897.9	279-350
Isobutane	C ₄ H ₁₀	58.12	g	1	°C	74.06	32.95	-25.20	77.57	0-1200
n-Butane	C ₄ H ₁₀	58.12	g	1	°C	89.46	30.13	-18.91	49.87	0-1200
Isobutene	C ₄ H ₈	56.10	g	1	°C	92.30	27.88	-15.47	34.98	0-1200
Calcium carbide	CaC ₂	64.10	c	2	K	82.88	25.64	-17.27	50.50	0-1200
Calcium carbonate	CaCO ₃	100.09	c	2	K	68.62	1.19	-8.66 × 10 ¹⁰	—	298-720
Calcium hydroxide	Ca(OH) ₂	74.10	c	1	K	82.34	4.975	-12.87 × 10 ¹⁰	—	273-1033
Calcium oxide	CaO	56.08	c	2	K	89.5				276-373
Carbon	C	12.01	c [†]	2	K	41.84	2.03	-4.52 × 10 ¹⁰		10273-1173
Carbon dioxide	CO ₂	44.01	g	1	°C	11.18	1.095	-4.891 × 10 ¹⁰		273-1373
Carbon monoxide	CO	28.01	g	1	°C	36.11	4.233	-2.887	7.464	0-1500
Carbon tetrachloride	CCl ₄	153.84	l	1	K	28.95	0.4110	0.3548	-2.220	0-1500
Chlorine	Cl ₂	70.91	g	1	°C	12.285	0.01095	-318.26	3,425.2	273-343
Copper	Cu	63.54	c	1	K	33.60	1.367	-1.607	6.473	0-1200
					K	22.76	0.06117			273-1357

[†]Graphite. [‡]Rhombic. [§]Monoclinic. * (at 1 atm)

TABLE E.1 (cont.)

Compound	Formula	Mol. Wt.	State	Form	<i>T</i>	<i>a</i>	<i>b</i> · 10 ²	<i>c</i> · 10 ⁵	<i>d</i> · 10 ⁹	Temp. Range (in <i>T</i>)
Cumene (Isopropyl benzene)	C ₉ H ₁₂	120.19	g	1	°C	139.2	53.76	-39.79	120.5	0-1200
Cyclohexane	C ₆ H ₁₂	84.16	g	1	°C	94.140	49.62	-31.90	80.63	0-1200
Cyclopentane	C ₅ H ₁₀	70.13	g	1	°C	73.39	39.28	-25.54	68.66	0-1200
Ethane	C ₂ H ₆	30.07	g	1	°C	49.37	13.92	-5.816	7.280	0-1200
Ethyl alcohol	C ₂ H ₆ O	46.07	l	1	K	-325.137	0.041379	-1.403.1	1.7035 × 10 ⁴	250-400
			g	1	°C	61.34	15.72	-8.749	19.83	0-1200
Ethylene	C ₂ H ₄	28.05	g	1	°C	40.75	11.47	-6.891	17.66	0-1200
Ferric oxide	Fe ₂ O ₃	159.70	c	2	K	103.4	6.711	-17.72 × 10 ¹⁰	—	273-1097
Formaldehyde	CH ₂ O	30.03	g	1	°C	34.28	4.268	0.0000	-8.694	0-1200
Helium	He	4.00	g	1	°C	20.8				All
<i>n</i> -Hexane	C ₆ H ₁₄	86.17	l	1	K	31.421	0.97606	-235.37	3,092.7	273-400
			g	1	°C	137.44	40.85	-23.92	57.66	0-1200
Hydrogen	H ₂	2.016	g	1	°C	28.84	0.00765	0.3288	-0.8698	0-1500
Hydrogen bromide	HBr	80.92	g	1	°C	29.10	-0.0227	0.9887	-4.858	0-1200
Hydrogen chloride	HCl	36.47	g	1	°C	29.13	-0.1341	0.9715	-4.335	0-1200
Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	2.908	1.092		0-1200
Hydrogen sulfide	H ₂ S	34.08	g	1	°C	33.51	1.547	0.3012	-3.292	0-1500
Magnesium chloride	MgCl ₂	95.23	c	1	K	72.4	1.58			273-991
Magnesium oxide	MgO	40.32	c	2	K	45.44	0.5008	-8.732 × 10 ¹⁰		273-2073
Methane	CH ₄	16.04	g	1	°C	34.31	5.469	0.3661	-11.00	0-1200
			g	1	K	19.87	5.021	1.268	-11.00	273-1500
Methyl alcohol	CH ₃ OH	32.04	l	1	K	-259.25	0.03358	-1.1639	1.4052 × 10 ⁴	273-400
			g	1	°C	42.93	8.301	-1.87	-8.03	0-700
Methyl cyclohexane	C ₇ H ₁₄	98.18	g	1	°C	121.3	56.53	-37.72	100.8	0-1200
Methyl cyclopentane	C ₆ H ₁₂	84.16	g	1	°C	98.83	45.857	-30.44	83.81	0-1200
Nitric acid	HNO ₃	63.02	l	1	°C	110.0				25

Nitric oxide	NO	30.01	g	1	°C	29.50	0.8188	-0.2925	0.3652	0-3500
Nitrogen	N ₂	28.02	g	1	°C	29.00	0.2199	0.5723	-2.871	0-1500
Nitrogen dioxide	NO ₂	46.01	g	1	°C	36.07	3.97	-2.88	7.87	0-1200
Nitrogen tetroxide	N ₂ O ₄	92.02	g	1	°C	75.7	12.5	-11.3		0-300
Nitrous oxide	N ₂ O	44.02	g	1	°C	37.66	4.151	-2.694	10.57	0-1200
Oxygen	O ₂	32.00	g	1	°C	29.10	1.158	-0.6076	1.311	0-1500
n-Pentane	C ₅ H ₁₂	72.15	l	1	K	33.24	192.41	-236.87	17,944	270-350
Propane	C ₃ H ₈	44.09	g	1	°C	114.8	34.09	-18.99	42.26	0-1200
Propylene	C ₃ H ₆	42.08	g	1	°C	68.032	22.59	-13.11	31.71	0-1200
Sodium carbonate	Na ₂ CO ₃	105.99	c	1	°C	59.580	17.71	-10.17	24.60	0-1200
Sodium carbonate	Na ₂ CO ₃ · 10H ₂ O	286.15	c	1	K	535.6				288-371
										298
Sulfur	S	32.07	c [‡]	1	K	15.2	2.68			273-368
			c [§]	1	K	18.5	1.84			368-392
Sulfuric acid	H ₂ SO ₄	98.08	l	1	°C	139.1	15.59			10-45
Sulfur dioxide	SO ₂	64.07	g	1	°C	38.91	3.904	-3.104	8.606	0-1500
Sulfur trioxide	SO ₃	80.07	g	1	°C	48.50	9.188	-8.540	32.40	0-1000
Toluene	C ₇ H ₈	92.13	l	1	K	1.8083	81.222	-151.27	1,630	270-370
			g	1	°C	94.18	38.00	-27.86	80.33	0-1200
Water	H ₂ O	18.016	l	1	K	18.2964	47.212	-133.88	1,314.2	273-373
			g	1	°C	33.46	0.6880	0.7604	-3.593	0-1500

[†]Graphite. [‡]Rhombic. [§]Monoclinic.

APPENDIX F

HEATS OF FORMATION AND COMBUSTION

TABLE F.1 Heats of Formation and Heats of Combustion of Compounds at 25°C*

Standard states of products for $\Delta\hat{H}_c^\circ$ are $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{N}_2(\text{g})$, $\text{SO}_2(\text{g})$, and $\text{HCl}(\text{aq})$. To convert to Btu/lb mol, multiply by 430.6.

Compound	Formula	Mol. wt.	State	$\Delta\hat{H}_f^\circ$ (kJ/g mol)	$\Delta\hat{H}_c^\circ$ (kJ/g mol)
Acetic acid	CH_3COOH	60.05	l	-486.2	-871.69
			g		-919.73
Acetaldehyde	CH_3CHO	40.052	g	-166.4	-1192.36
Acetone	$\text{C}_3\text{H}_6\text{O}$	58.08	aq, 200	-410.03	
			g	-216.69	-1821.38
Acetylene	C_2H_2	26.04	g	226.75	-1299.61
Ammonia	NH_3	17.032	l	-67.20	
			g	-46.191	-382.58
Ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$	96.09	c		
			aq	-941.86	
Ammonium chloride	NH_4Cl	53.50	c	-315.4	
Ammonium hydroxide	NH_4OH	35.05	aq	-366.5	
Ammonium nitrate	NH_4NO_3	80.05	c	-366.1	
			aq	-339.4	
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	132.15	c	-1179.3	
			aq	-1173.1	
Benzaldehyde	$\text{C}_6\text{H}_5\text{CHO}$	106.12	l	-88.83	
			g	-40.0	

TABLE F.1 (cont.)

Compound	Formula	Mol. wt.	State	$\Delta\hat{H}_f^\circ$ (kJ/g mol)	$\Delta\hat{H}_c^\circ$ (kJ/g mol)
Benzene	C_6H_6	78.11	l	48.66	-3267.6
			g	82.927	-3301.5
Boron oxide	B_2O_3	69.64	c	-1263	
			l	-1245.2	
Bromine	Br_2	159.832	l	0	
			g	30.7	
<i>n</i> -Butane	C_4H_{10}	58.12	l	-147.6	-2855.6
			g	-124.73	-2878.52
Isobutane	C_4H_{10}	58.12	l	-158.5	-2849.0
			g	-134.5	-2868.8
1-Butene	C_4H_8	56.104	g	1.172	-2718.58
Calcium arsenate	$Ca_3(AsO_4)_2$	398.06	c	-3330.5	
Calcium carbide	CaC_2	64.10	c	-62.7	
Calcium carbonate	$CaCO_3$	100.09	c	-1206.9	
Calcium chloride	$CaCl_2$	110.99	c	-794.9	
Calcium cyanamide	$CaCN_2$	80.11	c	-352	
Calcium hydroxide	$Ca(OH)_2$	74.10	c	-986.56	
Calcium oxide	CaO	56.08	c	-635.6	
Calcium phosphate	$Ca_3(PO_4)_2$	310.19	c	-4137.6	
Calcium silicate	$CaSiO_3$	116.17	c	-1584	
Calcium sulfate	$CaSO_4$	136.15	c	-1432.7	
			aq	-1450.5	
Calcium sulfate (gypsum)	$CaSO_4 \cdot 2H_2O$	172.18	c	-2021.1	
Carbon	C	12.01	c	0	-393.51
			Graphite (β)		
Carbon dioxide	CO_2	44.01	g	-393.51	
			l	-412.92	
Carbon disulfide	CS_2	76.14	l	87.86	-1075.2
			g	115.3	-1102.6
Carbon monoxide	CO	28.01	g	-110.52	-282.99
Carbon tetrachloride	CCl_4	153.838	l	-139.5	-352.2
			g	-106.69	-384.9
Chloroethane	C_2H_5Cl	64.52	g	-105.0	-1421.1
			l	-41.20	-5215.44
Cumene (isopropylbenzene)	$C_6H_5CH(CH_3)_2$	120.19	g	3.93	-5260.59
			c	-769.86	
Cupric sulfate	$CuSO_4$	159.61	aq	-843.12	
			c	-751.4	
Cyclohexane	C_6H_{12}	84.16	g	-123.1	-3953.0
Cyclopentane	C_5H_{10}	70.130	l	-105.8	-3290.9
			g	-77.23	-3319.5

TABLE F.1 (cont.)

Compound	Formula	Mol. wt.	State	$\Delta\hat{H}_f^\circ$ (kJ/g mol)	$\Delta\hat{H}_c^\circ$ (kJ/g mol)
Ethane	C_2H_6	30.07	g	-84.667	-1559.9
Ethyl acetate	$CH_3CO_2C_2H_5$	88.10	l	-442.92	-2274.48
Ethyl alcohol	C_2H_5OH	46.068	l	-277.63	-1366.91
			g	-235.31	-1409.25
Ethyl benzene	$C_6H_5 \cdot C_2H_5$	106.16	l	-12.46	-4564.87
			g	29.79	-4607.13
Ethyl chloride	C_2H_5Cl	64.52	g	-105	
Ethylene	C_2H_4	28.052	g	52.283	-1410.99
Ethylene chloride	C_2H_3Cl	62.50	g	31.38	-1271.5
3-Ethyl hexane	C_8H_{18}	114.22	l	-250.5	-5470.12
			g	-210.9	-5509.78
Ferric chloride	$FeCl_3$		c	-403.34	
Ferric oxide	Fe_2O_3	159.70	c	-822.156	
Ferric sulfide	FeS_2	<i>see Iron sulfide</i>		<i>see Iron sulfide</i>	
Ferrosoferric oxide	Fe_3O_4	231.55	c	-1116.7	
Ferrous chloride	$FeCl_2$		c	-342.67	-303.76
Ferrous oxide	FeO	71.85	c	-267	
Ferrous sulfide	FeS	87.92	c	-95.06	
Formaldehyde	H_2CO	30.026	g	-115.89	-563.46
<i>n</i> -Heptane	C_7H_{16}	100.20	l	-224.4	-4816.91
			g	-187.8	-4853.48
<i>n</i> -Hexane	C_6H_{14}	86.17	l	-198.8	-4163.1
			g	-167.2	-4194.753
Hydrogen	H_2	2.016	g	0	-285.84
Hydrogen bromide	HBr	80.924	g	-36.23	
Hydrogen chloride	HCl	36.465	g	-92.311	
Hydrogen cyanide	HCN	27.026	g	130.54	
Hydrogen sulfide	H_2S	34.082	g	-20.15	-562.589
Iron sulfide	FeS_2	119.98	c	-177.9	
Lead oxide	PbO	223.21	c	-219.2	
Magnesium chloride	$MgCl_2$	95.23	c	-641.83	
Magnesium hydroxide	$Mg(OH)_2$	58.34	c	-924.66	
Magnesium oxide	MgO	40.32	c	-601.83	
Methane	CH_4	16.041	g	-74.84	-890.4
Methyl alcohol	CH_3OH	32.042	l	-238.64	-726.55
			g	-201.25	-763.96
Methyl chloride	CH_3Cl	50.49	g	-81.923	-766.63 [†]
Methyl cyclohexane	C_7H_{14}	98.182	l	-190.2	-4565.29
			g	-154.8	-4600.68
Methyl cyclopentane	C_6H_{12}	84.156	l	-138.4	-3937.7
			g	-106.7	-3969.4

TABLE F.1 (cont.)

Compound	Formula	Mol. wt.	State	$\Delta\hat{H}_f^\circ$ (kJ/g mol)	$\Delta\hat{H}_c^\circ$ (kJ/g mol)
Nitric acid	HNO_3	63.02	l	-173.23	
			aq	-206.57	
Nitric oxide	NO	30.01	g	90.374	
Nitrogen dioxide	NO_2	46.01	g	33.85	
Nitrous oxide	N_2O	44.02	g	81.55	
<i>n</i> -Pentane	C_5H_{12}	72.15	l	-173.1	-3509.5
			g	-146.4	-3536.15
Phosphoric acid	H_3PO_4	98.00	c	-1281	
			aq (1H ₂ O)	-1278	
Phosphorus	P_4	123.90	c	0	
Phosphorus pentoxide	P_2O_5	141.95	c	-1506	
Propane	C_3H_8	44.09	l	-119.84	-2204.0
			g	-103.85	-2220.0
Propene	C_3H_6	42.078	g	20.41	-2058.47
<i>n</i> -Propyl alcohol	$\text{C}_3\text{H}_8\text{O}$	60.09	g	-255	-2068.6
<i>n</i> -Propylbenzene	$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{C}_2\text{H}_5$	120.19	l	-38.40	-5218.2
			g	7.824	-5264.5
Silicon dioxide	SiO_2	60.09	c	-851.0	
Sodium bicarbonate	NaHCO_3	84.01	c	-945.6	
Sodium bisulfate	NaHSO_4	120.07	c	-1126	
Sodium carbonate	Na_2CO_3	105.99	c	-1130	
Sodium chloride	NaCl	58.45	c	-411.00	
Sodium cyanide	NaCN	49.01	c	-89.79	
Sodium nitrate	NaNO_3	85.00	c	-466.68	
Sodium nitrite	NaNO_2	69.00	c	-359	
Sodium sulfate	Na_2SO_4	142.05	c	-1384.5	
Sodium sulfide	Na_2S	78.05	c	-373	
Sodium sulfite	Na_2SO_3	126.05	c	-1090	
Sodium thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3$	158.11	c	-1117	
Sulfur	S	32.07	c	0	
			(rhombic)		
			c	0.297	
			(monoclinic)		
Sulfur chloride	S_2Cl_2	135.05	l	-60.3	
Sulfur dioxide	SO_2	64.066	g	-296.90	
Sulfur trioxide	SO_3	80.066	g	-395.18	
Sulfuric acid	H_2SO_4	98.08	l	-811.32	
			aq	-907.51	
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	92.13	l	11.99	-3909.9
			g	50.000	-3947.9

TABLE F.1 (cont.)

Compound	Formula	Mol. wt.	State	$\Delta\hat{H}_f^\circ$ (kJ/g mol)	$\Delta\hat{H}_c^\circ$ (kJ/g mol)
Water	H ₂ O	18.016	l	-285.840	
			g	-241.826	
<i>m</i> -Xylene	C ₆ H ₄ (CH ₃) ₂	106.16	l	-25.42	-4551.86
			g	17.24	-4594.53
<i>o</i> -Xylene	C ₆ H ₄ (CH ₃) ₂	106.16	l	-24.44	-4552.86
			g	19.00	-4596.29
<i>p</i> -Xylene	C ₆ H ₄ (CH ₃) ₂	106.16	l	-24.43	-4552.86
			g	17.95	-4595.25
Zinc sulfate	ZnSO ₄	161.45	c	-978.55	
			aq	-1059.93	

*Sources of data are given at the beginning of Appendix D, References 1, 4, and 5.

†Standard state HCl(g).

APPENDIX G

VAPOR PRESSURES

TABLE G.1 Vapor Pressures of Various Substances

Antoine equation:

$$\ln(p^*) = A - \frac{B}{C + T}$$

where p^* = vapor pressure, mm Hg

T = temperature, K

A, B, C = constants

Name	Formula	Range (K)	A	B	C
Acetic acid	$C_2H_4O_2$	290–430	16.8080	3405.57	–56.34
Acetone	C_3H_6O	241–350	16.6513	2940.46	–35.93
Ammonia	NH_3	179–261	16.9481	2132.50	–32.98
Benzene	C_6H_6	280–377	15.9008	2788.51	–52.36
Carbon disulfide	CS_2	288–342	15.9844	2690.85	–31.62
Carbon tetrachloride	CCl_4	253–374	15.8742	2808.19	–45.99
Chloroform	$CHCl_3$	260–370	15.9732	2696.79	–46.16
Cyclohexane	C_6H_{12}	280–380	15.7527	2766.63	–50.50
Ethyl acetate	$C_4H_8O_2$	260–385	16.1516	2790.50	–57.15
Ethyl alcohol	C_2H_6O	270–369	18.5242	3578.91	–50.50
Ethyl bromide	C_2H_5Br	226–333	15.9338	2511.68	–41.44
<i>n</i> -Heptane	C_7H_{16}	270–400	15.8737	2911.32	–56.51
<i>n</i> -Hexane	C_6H_{14}	245–370	15.8366	2697.55	–48.78
Methyl alcohol	CH_4O	257–364	18.5875	3626.55	–34.29
<i>n</i> -Pentane	C_5H_{12}	220–330	15.8333	2477.07	–39.94
Sulfur dioxide	SO_2	195–280	16.7680	2302.35	–35.97
Toluene	$C_6H_5CH_3$	280–410	16.0137	3096.52	–53.67
Water	H_2O	284–441	18.3036	3816.44	–46.13

SOURCE: R. C. Reid, J. M. Prausnitz, and T. K. Sherwood. *The Properties of Gases and Liquids*, 3rd ed., Appendix A. New York: McGraw-Hill (1977).

APPENDIX H

HEATS OF SOLUTION AND DILUTION

TABLE H.1 Integral Heats of Solution and Dilution at 25°C

Formula	Description	State	$-\Delta\hat{H}_f^\circ$ (kJ/g mol)	$-\Delta\hat{H}_{\text{soln}}^\circ$ (kJ/g mol)	$-\Delta\hat{H}_{\text{dil}}^\circ$ (kJ/g mol)
NaOH	crystalline II		426.726		
	in 3 H ₂ O	aq	455.612	28.869	28.869
	4 H ₂ O	aq	461.156	34.434	5.564
	5 H ₂ O	aq	464.486	37.739	3.305
	10 H ₂ O	aq	469.227	42.509	4.769
	20 H ₂ O	aq	469.591	42.844	.334
	30 H ₂ O	aq	469.457	42.718	.125
	40 H ₂ O	aq	469.340	42.593	.125
	50 H ₂ O	aq	469.252	42.509	.083
	100 H ₂ O	aq	469.059	42.342	.167
	200 H ₂ O	aq	469.026	42.258	.083
	300 H ₂ O	aq	469.047	42.300	.041
	500 H ₂ O	aq	469.097	42.383	.083
	1,000 H ₂ O	aq	469.189	42.467	.083
	2,000 H ₂ O	aq	469.285	42.551	.083
	10,000 H ₂ O	aq	469.448	42.718	.041
	50,000 H ₂ O	aq	469.528	42.802	.083
	∞ H ₂ O	aq	469.595	42.886	.083
H ₂ SO ₄		liq	811.319		
	in 0.5 H ₂ O	aq	827.051	15.731	15.731
	1.0 H ₂ O	aq	839.394	28.074	12.343
	1.5 H ₂ O	aq	848.222	36.902	8.823
	2 H ₂ O	aq	853.243	41.923	5.021
	3 H ₂ O	aq	860.314	48.994	7.071
	4 H ₂ O	aq	865.376	54.057	5.063
	5 H ₂ O	aq	869.351	58.032	3.975
	10 H ₂ O	aq	878.347	67.027	8.995
	25 H ₂ O	aq	883.618	72.299	5.272
	50 H ₂ O	aq	884.664	73.345	1.046
	100 H ₂ O	aq	885.292	73.973	0.628
	500 H ₂ O	aq	888.054	76.734	2.761
	1,000 H ₂ O	aq	889.894	78.575	1.841
	10,000 H ₂ O	aq	898.388	87.069	2.636
	100,000 H ₂ O	aq	904.957	93.637	6.568
	500,000 H ₂ O	aq	906.630	95.311	1.674
	∞ H ₂ O	aq	907.509	96.190	0.879

SOURCE: F. D. Rossini et al. "Selected Values of Chem. Thermo. Properties." *National Bureau of Standards Circular 500*. Washington, DC: U.S. Government Printing Office, 1952.

APPENDIX I

ENTHALPY- CONCENTRATION DATA

TABLE I.1 Enthalpy-Concentration Data for the Single-Phase Liquid Region and also the Saturated Vapor of the Acetic Acid-Water System at 1 Atmosphere
Reference state: Liquid water at 32°F and 1 atm; solid acid at 32°F and 1 atm.

Liquid or Vapor		Enthalpy—Btu/lb Liquid Solution						Enthalpy Saturated Vapor Btu/lb
Mole Fraction Water	Weight Fraction Water	20°C 68°F	40°C 104°F	60°C 140°F	80°C 176°F	100°C 212°F	Saturated Liquid	
0.00	0.0	93.54	111.4	129.9	149.1	169.0	187.5	361.8
0.05	0.01555	93.96	112.2	130.9	150.4	170.6	186.9	
0.10	0.03225	93.82	112.3	131.5	151.3	172.0	186.5	374.6
0.20	0.0698	92.61	111.9	131.7	152.2	173.8	185.2	395.3
0.30	0.1140	90.60	110.7	131.3	152.6	175.0	183.8	423.7
0.40	0.1667	87.84	108.9	130.6	152.6	176.1	182.9	461.4
0.50	0.231	83.96	106.3	129.1	152.7	177.1	182.4	510.5
0.55	0.268	81.48	104.5	128.1	152.5	177.5	182.3	
0.60	0.3105	78.53	102.5	126.9	152.1	178.0	182.0	573.4
0.65	0.358	75.36	100.2	125.5	151.6	178.3	181.9	
0.70	0.412	71.72	97.71	123.9	151.1	178.8	181.7	656.0
0.75	0.474	67.59	94.73	122.2	149.9	179.3	182.1	
0.80	0.545	62.88	91.43	120.2	149.7	179.9	181.6	767.3
0.85	0.630	57.44	87.56	117.8	148.9	180.5	181.6	
0.90	0.730	51.03	83.02	115.1	147.8	180.8	181.7	921.6
0.95	0.851	43.74	77.65	111.7	146.4	181.2	181.5	
1.00	1.00	36.06	71.91	107.7	143.9	180.1	180.1	1150.4

SOURCE: Data calculated from miscellaneous literature sources and smoothed.

TABLE I.2 Vapor-Liquid Equilibrium Data for the Acetic Acid-Water System; Pressure = 1 Atmosphere

x Mole Fraction Water in the Liquid	y Mole Fraction Water in the Vapor
0.020	0.035
0.040	0.069
0.060	0.103
0.080	0.135
0.100	0.165
0.200	0.303
0.300	0.425
0.400	0.531
0.500	0.627
0.600	0.715
0.700	0.796
0.800	0.865
0.900	0.929
0.940	0.957
0.980	0.985

SOURCE: Data from L. W. Cornell and R. E. Montonna, *Ind. Eng. Chem.*, 25, 1331-1335 (1933).

The following charts also have been placed in the CD that accompanies this book so that they can be expanded for better accuracy.

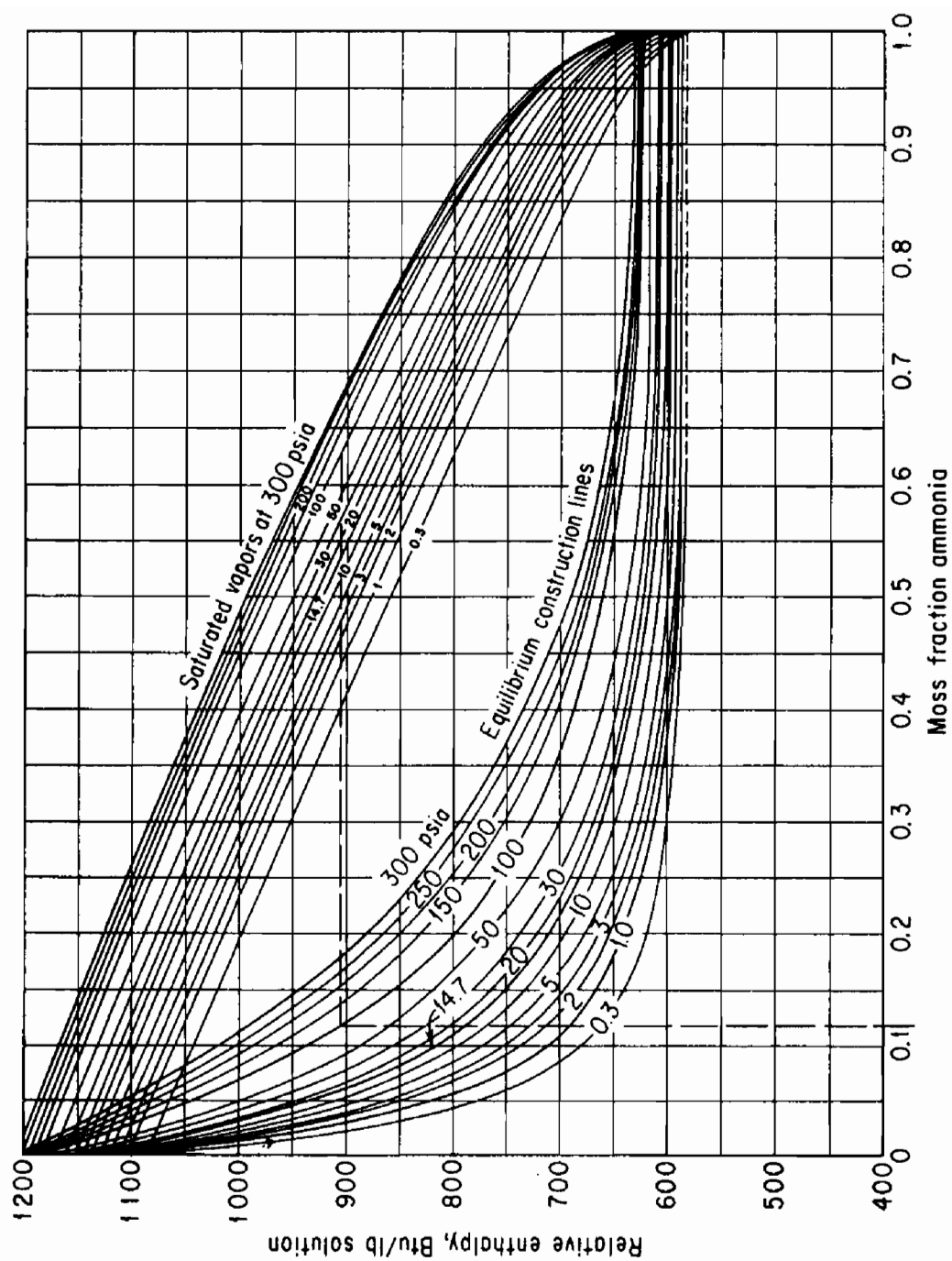


Figure I.1 Enthalpy-concentration chart for $\text{NH}_3\text{-H}_2\text{O}$

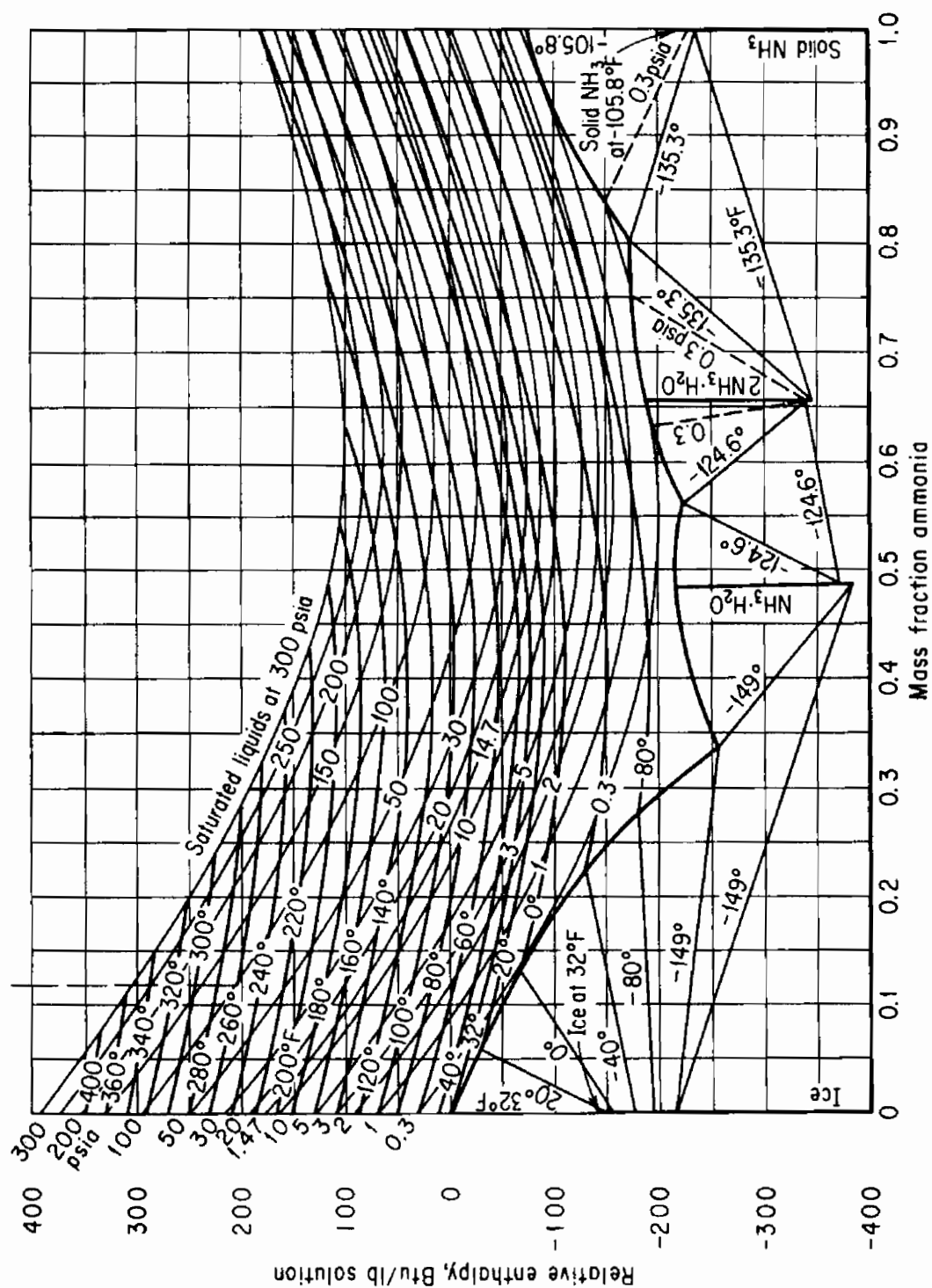


Figure I.1 (cont.)

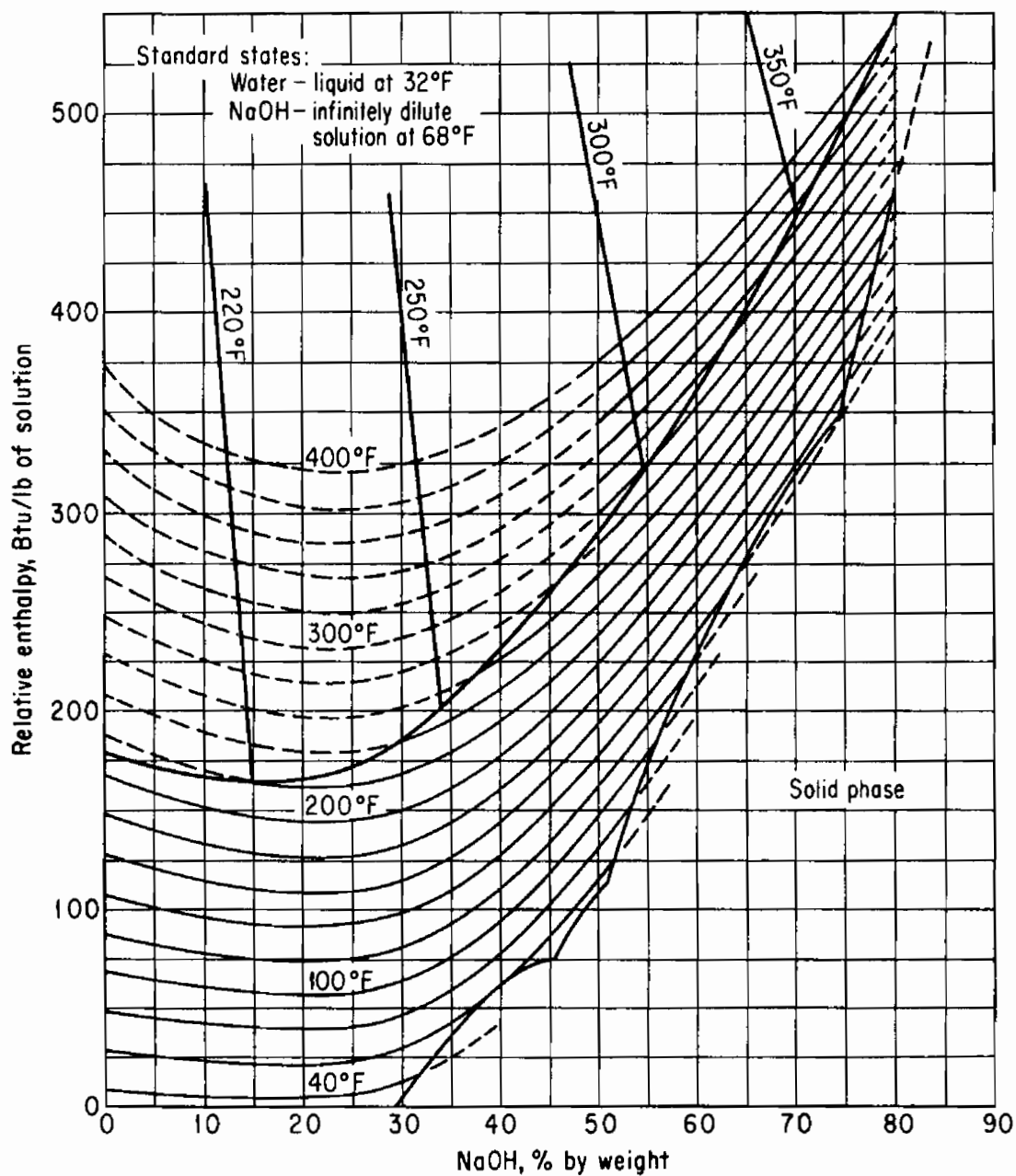


Figure I.2 Enthalpy-concentration chart for sodium hydroxide-water.

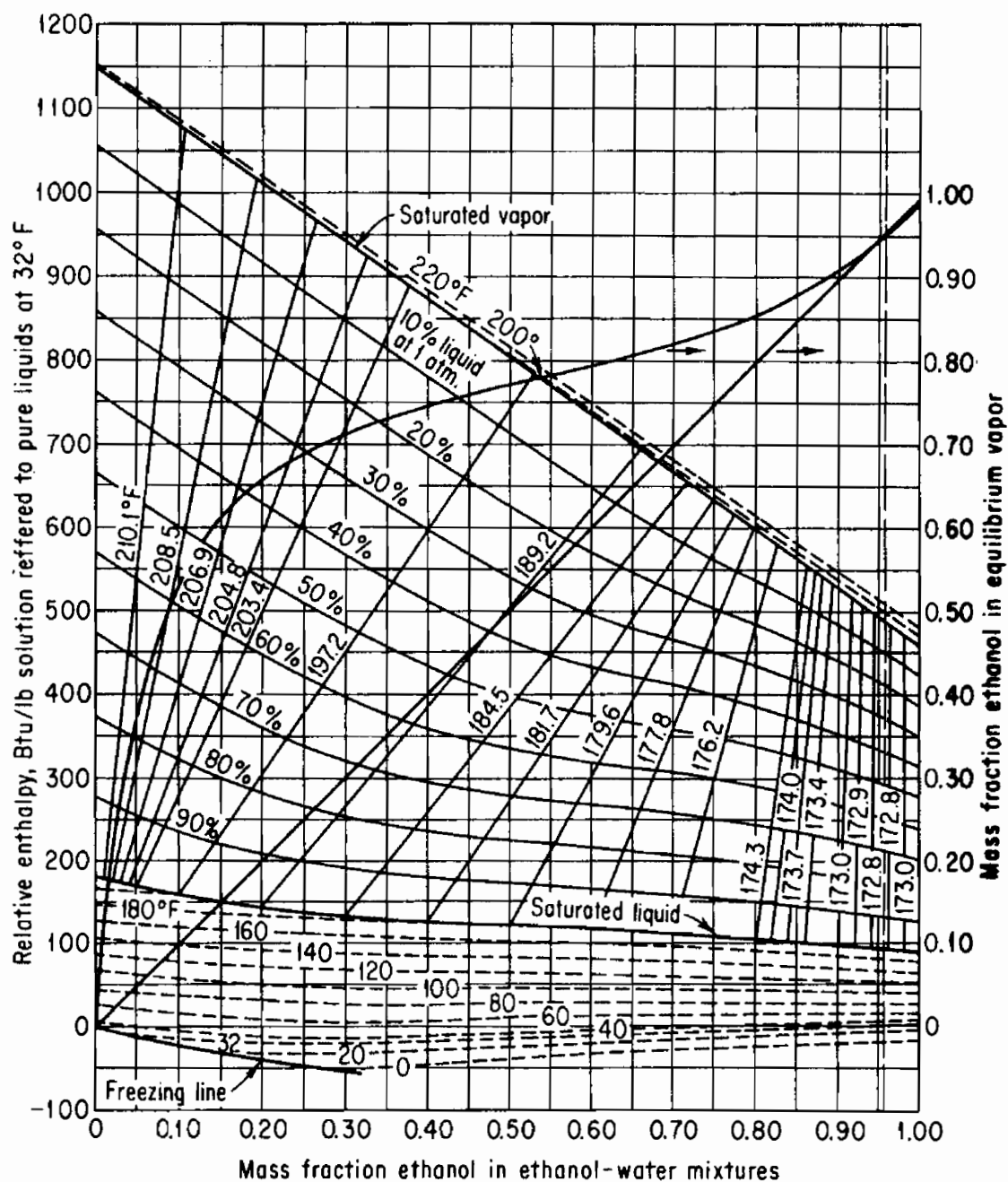


Figure I.3 Enthalpy-composition diagram for the ethanol-water system, showing liquid and vapor phases in equilibrium at 1 atm.

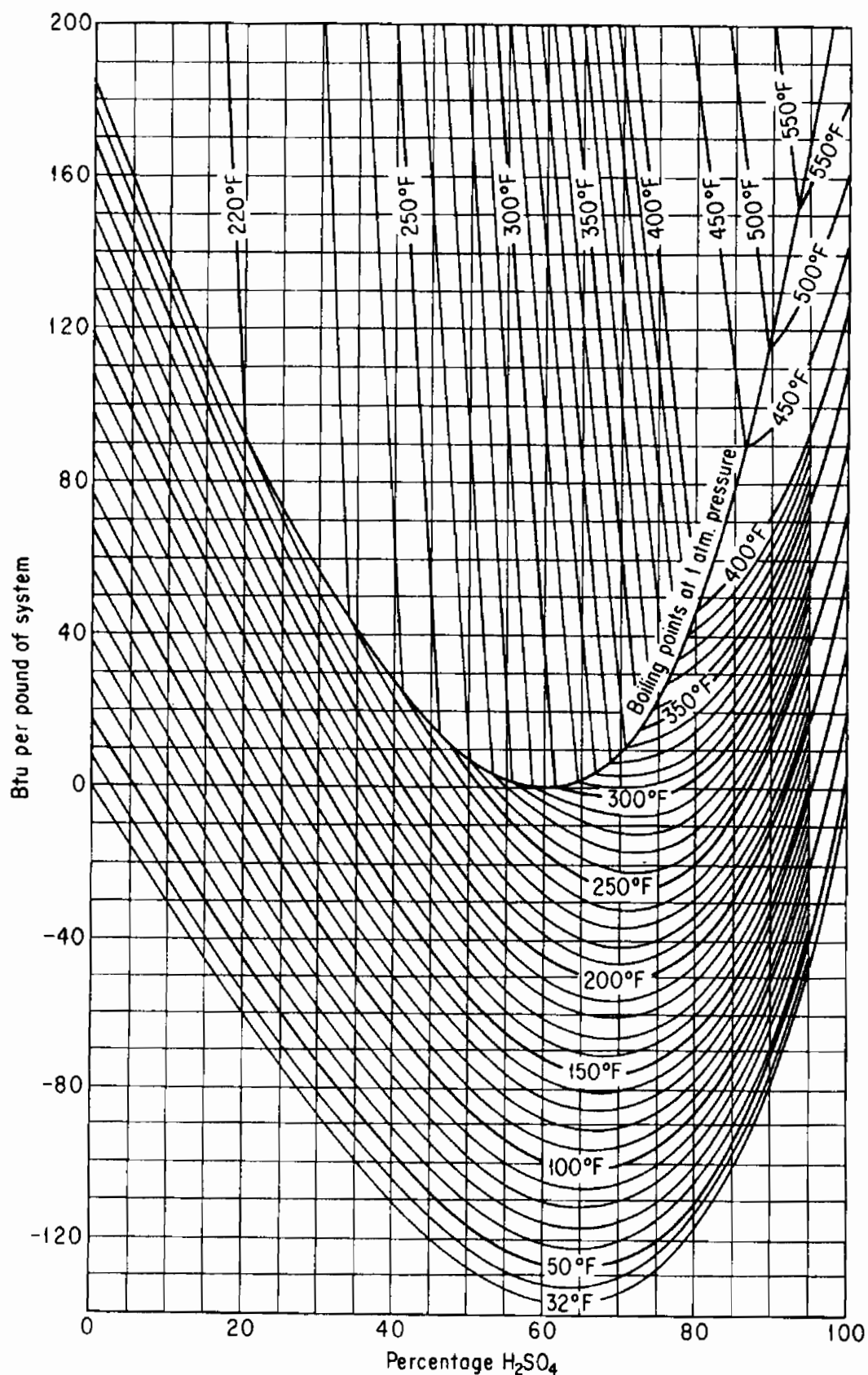


Figure I.4 Enthalpy-concentration of sulfuric acid-water system relative to pure components. (Water and H₂SO₄ at 32°F and own vapor pressure.) (Data from International Critical Tables, © 1943 O. A. Hougen and K. M. Watson.)

APPENDIX J

THERMODYNAMIC CHARTS

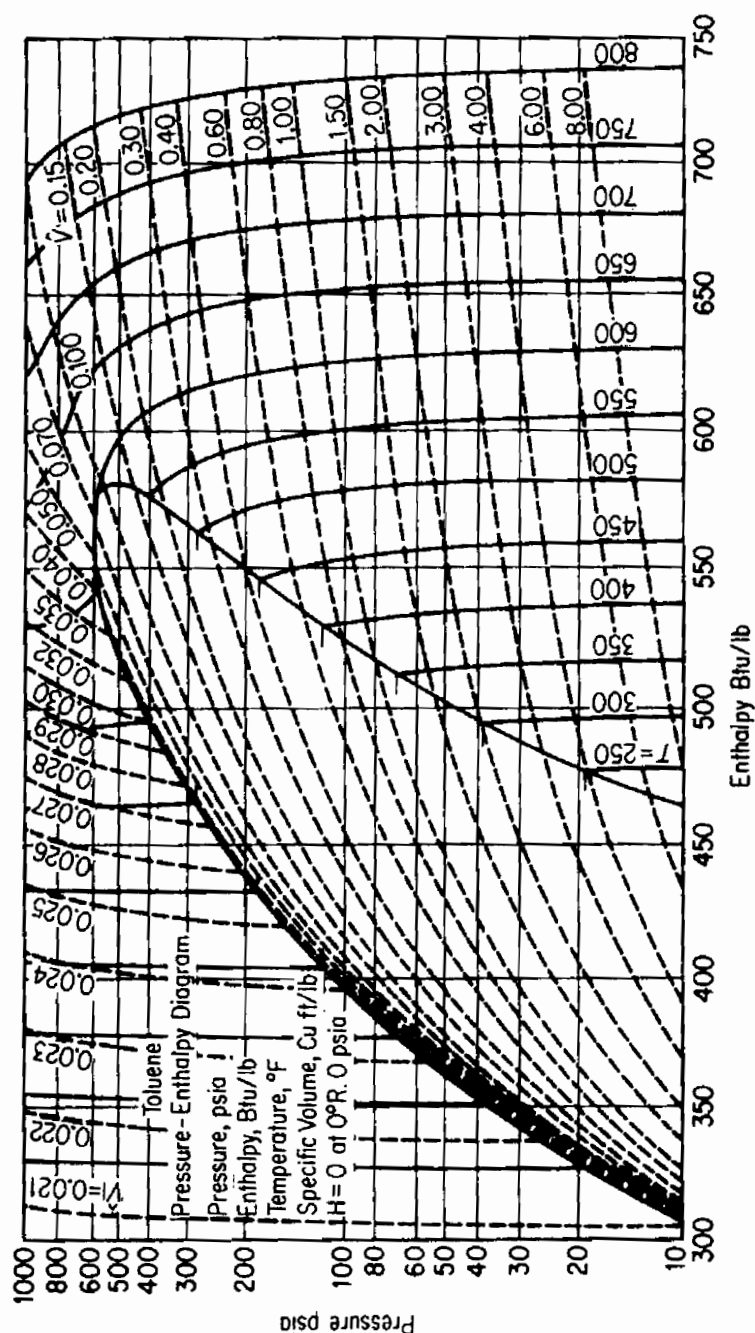


Figure J.1 Pressure-enthalpy chart for toluene.

The charts in Appendix J also have been placed in the CD that accompanies this book so that they can be expanded for better accuracy.

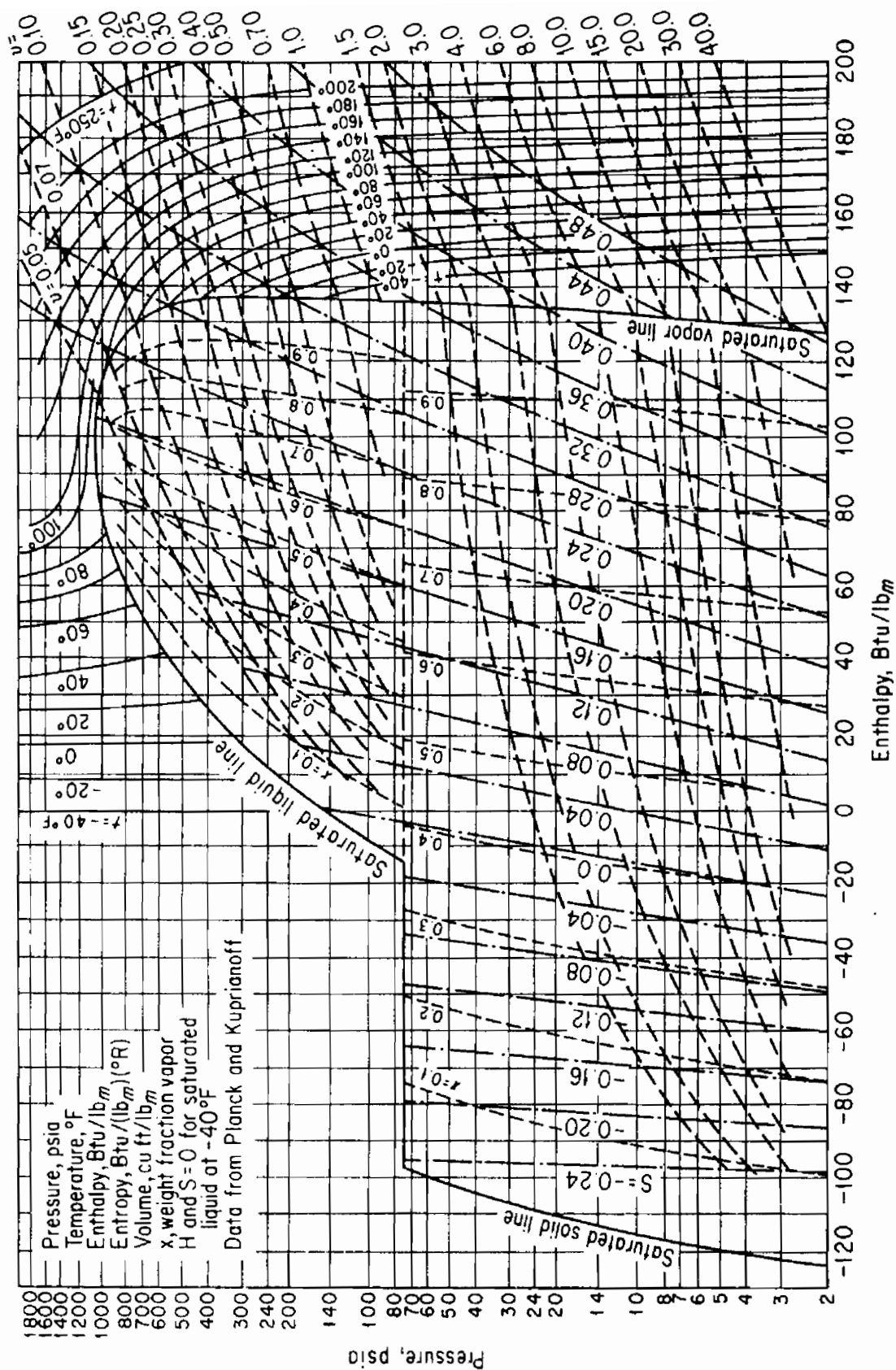


Figure J.2 Pressure-enthalpy chart for carbon dioxide.

PHYSICAL PROPERTIES OF PETROLEUM FRACTIONS

In the early 1930s, tests were developed that characterized petroleum oils and petroleum fractions so that various physical characteristics of petroleum products could be related to these tests. Details of the tests can be found in *Petroleum Products and Lubricants*, an annual publication of Committee D-2 of the American Society for Testing Materials.¹ These tests are not scientifically exact, and hence the procedure used in the tests must be followed faithfully if reliable results are to be obtained. However, the tests have been adopted because they are quite easy to perform in an ordinary laboratory and because the properties of petroleum fractions can be predicted from the results. The specifications for fuels, oils, and so on, are set out in terms of these tests plus many other properties, such as the flashpoint, the percent sulfur, and the viscosity.

Over the years various phases of the initial work have been extended and development of a new characterization scheme using the pseudocompound approach is evolving. Daubert² summarizes the traditional and new methods insofar as predicting molecular weights, pseudocritical temperature and pressure, acentric factor, and characterization factors.

In this appendix we present the results of the work of Smith and Watson and associates,³ who related petroleum properties to a factor known as the *characterization factor* (sometimes called the *UOP characterization factor*). It is defined as

$$K = \frac{(T_B)^{1/3}}{S}$$

where K = UOP characterization factor
 T = cubic average boiling point, °R
 S = specific gravity at 60°F/60°F

¹Report of Committee D-2, ASTM, Philadelphia, annually.

²T. E. Daubert. "Property Predictions." *Hydrocarbon Proc.*, 108–110 (March 1980).

³R. L. Smith and K. M. Watson. *Ind. Eng. Chem.*, 29, 1408 (1937); K. M. Watson and E. F. Nelson. *Ind. Eng. Chem.*, 25, 880 (1933); K. M. Watson, E. F. Nelson, and G. B. Murphy. *Ind. Eng. Chem.*, 27, 1460 (1935).

Other averages for boiling points are used in evaluating K and the other physical properties in the CD. (Refer to Daubert⁴ or Miquel⁵ for details.) This factor has been related to many of the other simple tests and properties of petroleum fractions such as viscosity, molecular weight, critical temperature, and percentage of hydrogen, so that it is quite easy to estimate the factor for any particular sample. Furthermore, tables of the UOP characterization factor are available for a wide variety of common types of petroleum fractions, as shown in Table K.1 for typical liquids.

TABLE K.1 Typical UOP Characterization Factors

Type of stock	K	Type of stock	K
Pennsylvania crude	12.2–12.5	Propane	14.7
Mid-continent crude	11.8–12.0	Hexane	12.8
Gulf Coast crude	11.0–11.8	Octane	12.7
East Texas crude	11.9	Natural gasoline	12.7–12.8
California crude	10.98–11.9	Light gas oil	10.5
Benzene	9.5	Kerosene	10.5–11.5

Refer to the CD for charts of the hydrocarbons that give (a) the specific heats, (b) the vapor pressure, (c) the heat of combustion, (d) the °API, and (e) the heats of vaporization.

⁴M. R. Riazi and T. E. Daubert. *Ind. Eng. Chem. Res.*, 26, 755–759 (1987).

⁵J. Miquel and F. Castells. *Hydrocarbon Processing*, 101–105 (Dec. 1993).

APPENDIX L

SOLUTION OF SETS OF EQUATIONS

This appendix contains a brief summary of methods of solving linear and nonlinear equations. It is only a summary; for details consult one of the numerous texts on numerical analysis that can be found in any library or one of the tutorials on the Internet.

L.1 Independent Linear Equations

1. What does the term “linear” mean?

The ease and accuracy of solving sets of equations often depends on whether the equations are linear or nonlinear. An equation is *linear* if it has

- (a) the property of proportionality, and
- (b) the property of superposition.

Let \mathcal{L} be a linear operator that causes a transformation of a variable x to another variable y . Then, for linearity

- (a) Proportionality occurs

$$y = \mathcal{L}(kx) = k \mathcal{L}(x)$$

- (b) Superposition occurs

$$y = \mathcal{L}(x_1 + x_2) = \mathcal{L}(x_1) + \mathcal{L}(x_2)$$

A term in an equation is deemed linear if the operation on the term is linear. Some examples of linear and nonlinear operators are:

Term	Classification	Example
$3x$	Linear	$3(x_1 + x_2) = 3x_1 + 3x_2$
Σx	Linear	$\Sigma(x_1 + x_2) = x_1 + x_2$
x^2	Nonlinear	$(x_1 + x_2)^2 \neq x_1^2 + x_2^2$
$\ln(x)$	Nonlinear	$\ln(x_1 + x_2) \neq \ln(x_1) + \ln(x_2)$

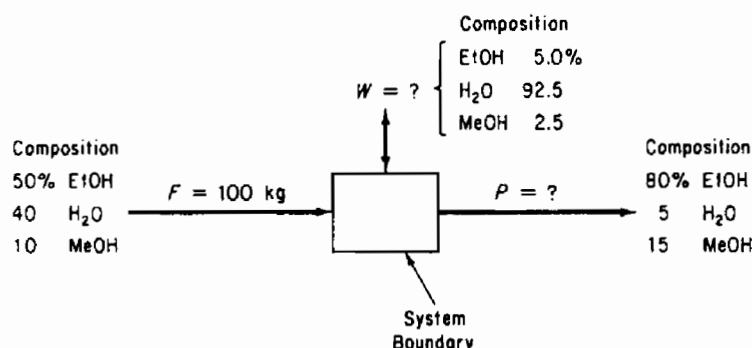


Figure L1 Data for material balances in a process.

2. What does the term “linear equation” mean?

A linear equation is an equation in which the sum of all the terms equal zero, and each term in the equation is itself linear. For example, Figure L1 displays a process.

The material balances for the process are:

$$\begin{aligned} 0.50(100) &= 0.80(P) + 0.05(W) \\ 0.40(100) &= 0.05(P) + 0.925(W) \\ 0.10(100) &= 0.15(P) + 0.025(W) \end{aligned} \quad (\text{L.1})$$

In general, if you write several *linear* material balances, say m in number, they will take the form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \dots + a_{2n}x_n &= b_2 \\ &\dots \\ a_{m1}x_1 + a_{m2}x_2 + \dots + a_{mn}x_n &= b_m \end{aligned} \quad (\text{L.2})$$

or in compact matrix notation

$$\mathbf{Ax} = \mathbf{b} \quad (\text{L.2a})$$

where x_1, x_2, \dots, x_n represent the unknown variables, and a_{ij} and b_i represent the constants and known variables.

3. What does the term “set of independent equations” mean?

You know that if you add two equations together to get a third equation, the set of three equations is said to be *not independent*; they are said to be *dependent*. Only two of the equations, any two, are said to be independent because you can formulate the third equation from the other two. Formally, linear equations are said to be independent if the sum of each equation multiplied by its related coefficient is equal to zero only if all of the coefficients are equal to zero. In symbols this means

$$c_1 (\text{Eq. 1}) + c_2 (\text{Eq. 2}) + \dots + c_n (\text{Eq. N}) = 0 \quad (\text{L.3})$$

For example, are the following equations independent?

$$\begin{aligned} 3x_1 + 4x_2 &= 0 \\ x_1 - 3x_2 &= 0 \end{aligned}$$

According to Equation (L3), you inquire if

$$c_1 (3x_1 + 4x_2) + c_2 (x_1 - 3x_2) = 0 \quad (\text{L.4})$$

for any x_i and any values of c_i other than each $c_i = 0$? The answer is no. Multiply the terms out in Equation (L4), and rearrange to get a better perspective

$$x_1 (3c_1 + c_2) + x_2 (4c_1 - 3c_2) = 0$$

Only $c_i = 0$ makes the equation valid for any x_i .

On the other hand, the following equations

$$\begin{aligned} y_1 &= 2x_1 - x_2 \\ y_2 &= x_1 + 2x_2 \\ y_3 &= x_1 + 4x_2 \end{aligned}$$

are not linearly independent because

$$c_1 (2x_1 - x_2) + c_2 (x_1 + 2x_2) + c_3 (x_1 + 4x_2) = 0$$

for at least one set of c_i 's, namely $c_1 = 1$, $c_2 = -9/2$, and $c_3 = 5/2$.

4. How can you tell if a set of linear equations are independent?

The explanation above does not provide a convenient way to determine whether a set of linear equations is comprised of independent equations. Two classical ways of determining independence are:

- (a) Determine the rank of the matrix **A** comprised of the coefficients of the equations, or
- (b) Determine the order of the largest nonzero determinant that exists for **A** (which is the same as the rank).

The rank is equal to the number of independent equations. We will use the rank in what follows because most software can compute the rank. Consult references on linear algebra for method (b). We advise using software to compute the rank of more than three equations to avoid error and save time.

In what follows we will employ the Gauss-Jordan elimination method of solving sets of linear equations to determine the rank of a matrix. If you use a computer program to solve equations like (L.2), you probably will not even be aware of the particular techniques that are used by the program.

The essence of the Gauss-Jordan method is to transform Equation (L.2) into Equation (L.5) by sequential nonunique elementary operations on Equation (L.2):

$$\begin{aligned}x_1 + 0 + \cdots + 0 &= b'_1 \\0 + x_2 + \cdots + 0 &= b'_2 \\&\vdots \\0 + 0 + \cdots + x_n &= b'_n\end{aligned}\tag{L.5}$$

Equation (L.5) has a solution for x_1, \dots, x_n that can be obtained by inspection, and the rank of the coefficient matrix is the number of rows that contain an x_i .

To illustrate the elementary operations that are required to execute the Gauss-Jordan method, consider the following set of three equations in three unknowns:

$$4x_1 + 2x_2 + x_3 = 15 \tag{1}$$

$$20x_1 + 5x_2 - 7x_3 = 0 \tag{2}$$

$$8x_1 - 3x_2 + 5x_3 = 24 \tag{3}$$

The augmented matrix includes the righthand side of the equations as elements of the fourth column.

$$\left[\begin{array}{ccc|c} 4 & 2 & 1 & 15 \\ 20 & 5 & -7 & 0 \\ 8 & -3 & 5 & 24 \end{array} \right]$$

Take the a_{11} element as a pivot. To make it 1 and the other elements in the first column zero, carry out the following elementary operations shown in order for each row:

- (a) Subtract $(\frac{20}{4}) \times$ Equation (1) from Equation (2).
- (b) Subtract $(\frac{8}{4}) \times$ Equation (1) from Equation (3)
- (c) Multiply Equation (1) by $\frac{1}{4}$.

to get

$$\left[\begin{array}{ccc|c} 1 & \frac{1}{2} & \frac{1}{4} & \frac{15}{4} \\ 0 & -5 & -12 & -75 \\ 0 & -7 & 3 & -6 \end{array} \right] \quad \begin{array}{l} \text{new Equation no.} \\ (1a) \\ (2a) \\ (3a) \end{array}$$

Carry out the following elementary operations to make the pivot element a_{22} equal to 1 and the other elements in the second column equal to zero:

- (d) Subtract $[(\frac{1}{2})/-5] \times \text{Equation (2a)}$ from Equation (1a).
- (e) Subtract $(-7/-5) \times \text{Equation (2a)}$ from Equation (3a).
- (f) Multiply Equation (2a) by $(1/-5)$.

to obtain

	<i>new Equation no.</i>
$\left[\begin{array}{ccc c} 1 & 0 & -\frac{19}{20} & -\frac{15}{4} \end{array} \right]$	(1b)
$\left[\begin{array}{ccc c} 0 & 1 & \frac{12}{5} & 15 \end{array} \right]$	(2b)
$\left[\begin{array}{ccc c} 0 & 0 & \frac{99}{5} & 99 \end{array} \right]$	(3b)

Another series of elementary operations (left for you to propose) leads to a 1 for the element a_{33} and zeros for the other two elements in the third column:

$$\left[\begin{array}{ccc|c} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 3 \\ 0 & 0 & 1 & 5 \end{array} \right]$$

The solution to the original set of equations is

$$\begin{aligned} x_1 &= 1 \\ x_2 &= 3 \\ x_3 &= 5 \end{aligned}$$

as can be observed using the augmentation column.

To obtain good accuracy and avoid numerical errors, the choice of the pivot should be made by scanning all the eligible coefficients and choosing the one with the greatest magnitude for the next pivot. For example, you might choose a_{21} for the first pivot, and then find that a_{31} would be the next pivot and finally a_{22} the last pivot to give

$$\left[\begin{array}{ccc|c} 0 & 1 & 0 & 3 \\ 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 5 \end{array} \right]$$

By exchanging rows 1 and 2, you get exactly the form as (L.5). The rank of the coefficient matrix is 3. Consequently, the equations are independent.

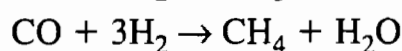
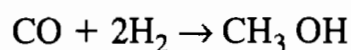
If the coefficient matrix had been reduced to

$$\left[\begin{array}{ccc|c} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array} \right]$$

then the rank of the coefficient matrix would be two, and only two of the equations would be independent.

5. How can you tell if several element balance equations are independent?

Before solving a set of element material balances, you should make sure the equations are independent. The procedure is as follows. Examine the two competing reactions:

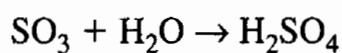


The number of elements involved is three: H, O, and C. Prepare a species matrix in which the rows (3) are the elements and the columns (5) are the chemical species:

$$\begin{array}{c} \text{H}_2 \quad \text{H}_2\text{O} \quad \text{CO} \quad \text{CH}_4 \quad \text{CH}_3\text{OH} \\ \begin{array}{l} \text{H} \\ \text{O} \\ \text{C} \end{array} \left[\begin{array}{ccccc} 2 & 2 & 0 & 4 & 4 \\ 0 & 1 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 & 1 \end{array} \right] \end{array}$$

Determine the rank of the species matrix. It is 3, thus three element balances will be independent.

The number of independent element balances is not always equal to the number of elements, as shown next. Consider the reaction



Form the species matrix and determine its rank.

$$\begin{array}{c} \text{H}_2\text{O} \quad \text{SO}_3 \quad \text{H}_2\text{SO}_4 \\ \begin{array}{l} \text{H} \\ \text{S} \\ \text{O} \end{array} \left[\begin{array}{ccc} 2 & 0 & 2 \\ 0 & 1 & 1 \\ 1 & 3 & 4 \end{array} \right] \end{array}$$

Make the transformation to

$$\begin{array}{c}
 \text{H}_2\text{O} \quad \text{SO}_3 \quad \text{H}_2\text{SO}_4 \\
 \begin{array}{l} \text{H} \\ \text{S} \\ \text{O} \end{array} \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & 0 \end{bmatrix}
 \end{array}$$

Note that the rank of the matrix is 2, not 3; hence only two independent element balances exist for independent material balances.

By inspection of the species matrix you can see that the elements in column 1 plus those in column 2 equal the elements in column 3 so that the column vectors are not independent.

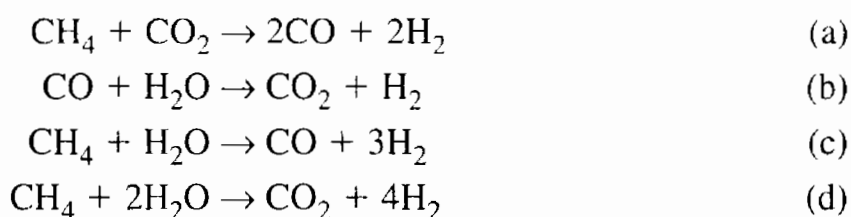
Note that the number of species (N) minus the number of independent element balances (the rank r of the species matrix) equals the number of independent reaction equations R

$$N - r = R$$

In Example 13.7, $N = 7$ and $r = 4$ so that $R = 7 - 4 = 3$ independent reaction equations.

6. How can you tell if several reaction equations are independent?

You can determine the number of independent reaction equations in a set by treating the equations as algebraic equations. Form the matrix of the coefficients in the equations (the coefficients on the lefthand side of the equation are defined to have negative values), and determine its rank. The rank is the number of independent reaction equations. For example, how many independent reaction equations exist in the following set:



The rank of the coefficient matrix

$$\begin{array}{l}
 \text{Eq. (a)} \\
 \text{Eq. (b)} \\
 \text{Eq. (c)} \\
 \text{Eq. (d)}
 \end{array}
 \begin{bmatrix}
 \text{CH}_4 & \text{CO}_2 & \text{CO} & \text{H}_2 & \text{H}_2\text{O} \\
 -1 & -1 & 2 & 2 & 0 \\
 0 & 1 & -1 & 1 & -1 \\
 -1 & 0 & 1 & 3 & -1 \\
 -1 & 1 & 0 & 4 & -2
 \end{bmatrix}$$

is just 2, hence only two of the equations are needed to form an independent set.

7. Solution of a set of linear independent equations

Look at Equation (L.2). With m equations in n unknown variables, three cases can be distinguished:

1. There is no set of x 's that satisfies Equation (L.2).
2. There is a unique set of x 's that satisfies Equation (L.2).
3. There is an infinite number of sets of x 's that satisfy Equation (L.2).

Figure L.2 represents each of the three cases geometrically in two dimensions. Case 1 is usually termed *inconsistent*, whereas cases 2 and 3 are consistent; but to an engineer who is interested in the solution of practical problems, case 3 is as unsatisfying as case 1. Hence case 2 will be termed *determinate*, and case 3 will be termed *indeterminate*.

To ensure that a system of equations represented by (L.2) has a unique solution, it is necessary to first show that (L.2) is *consistent*, that is, that the coefficient matrix \mathbf{A} and the augmented matrix $[\mathbf{A}, \mathbf{b}]$ must have the same *rank* r . Then, if $n = r$, the system (L.2) is *determinate*, whereas if $r < n$, as may be the case, then the number $(n - r)$ variables must be specified in some manner or determined by optimization procedures. If the equations are *independent*, $m = r$. In words, the number of independent equations in a set of equations equals the rank of the coefficient matrix of the equations. We use integers for simplicity as elements of the matrices in the examples below. Noninteger elements may lead to less clear results.

Let r = number of *independent* equations (the rank of the coefficient matrix)

n = number of variables whose values are unknown.

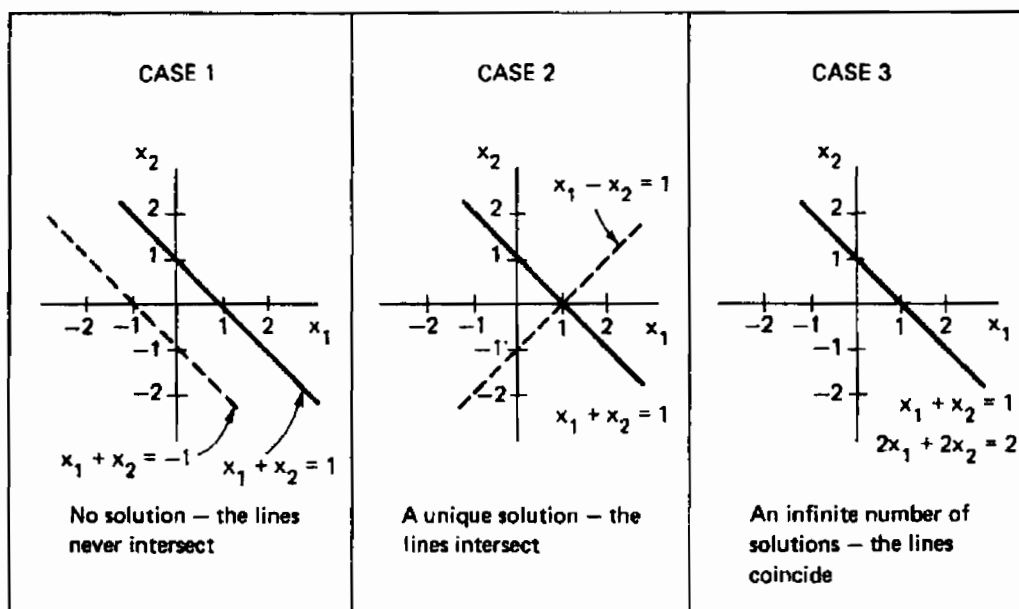


Figure L.2 Types of solutions of linear equations.

Homogenous Equations (all the righthand coefficients are zero) $Ax = 0$

$r = n$ The only solution is $x_1 = x_2 = \dots = 0$ (a unique solution but a trivial solution).

Example:

$$\left. \begin{array}{l} x_1 + x_2 - x_3 = 0 \\ 2x_1 + 4x_2 - x_3 = 0 \\ 3x_1 + 2x_2 + 2x_3 = 0 \end{array} \right\} \text{the only solution is } x_1 = x_2 = x_3 = 0$$

Using a computer code, you can find that the rank of the coefficient matrix is 3.

$r < n$ Multiple nonunique solutions exist.

Example 1:

$$\left. \begin{array}{l} x_1 + x_2 - x_3 = 0 \\ x_1 - 5x_2 - 3x_3 = 0 \end{array} \right\} \text{You can combine to get } 3x_2 + 2x_3 = 0, \text{ which has multiple solutions.}$$

The rank of the 2 by 3 coefficient matrix is 2, but $n = 3$, hence multiple solutions exist.

The rank of the augmented matrix is the same as the rank of A

Example 2:

$$\begin{array}{l} x_1 + x_2 - x_3 = 0 \\ 2x_1 - 3x_2 + x_3 = 0 \\ x_1 - 4x_2 + 2x_3 = 0 \end{array}$$

The rank of the coefficient matrix is 2, which is the same as the rank of the augmented matrix, but n still equals 3. Thus, multiple solutions exist.

$r > n$ Only the trivial solution exists.

$$\left. \begin{array}{l} x + y = 0 \\ x + 4y = 0 \\ 3x + 2y = 0 \end{array} \right\} \text{The only solution is the trivial solution } x = y = 0.$$

The rank of $A = \begin{bmatrix} 1 & 1 \\ 1 & 4 \\ 3 & 2 \end{bmatrix}$ is 2 and $n = 2$. The rank of the augmented matrix is also 2. A unique solution exists, but it is the trivial solution.

Nonhomogenous Equations $Ax = b$

$r = n$ A unique solution exists.

Example 1:

$$\begin{aligned} 2x_1 + x_2 - 2x_3 &= 0 \\ 3x_1 + 2x_2 + 2x_3 &= 1 \\ 5x_1 + 4x_2 + 3x_3 &= 4 \end{aligned} \quad \begin{array}{l} \text{3 equations, 3 variables, hence a solution} \\ \text{exists: } x_1 = 1, x_2 = 3, x_3 = -3 \end{array}$$

The rank of the coefficient matrix = 3; the augmented matrix has the same rank.

Example 2

$$\begin{aligned} x_1 + 2x_2 - 3x_3 &= 4 \\ x_1 + 3x_2 + x_3 &= 11 \\ 2x_1 + 5x_2 - 4x_3 &= 13 \\ 2x_1 + 6x_2 + 2x_3 &= 22 \end{aligned} \quad \begin{array}{l} \text{4 equations, 3 variables} \end{array}$$

The rank of the coefficient matrix is 3 (the maximum would be 3), and the rank of the augmented matrix is 3 (the maximum would be 4) so that a unique solution exists ($x_1 = 1, x_2 = 3, x_3 = 1$). Note that only 3 of the equations are independent.

Example 3:

$$\left. \begin{aligned} x_1 + 2x_2 - 3x_3 &= 1 \\ 3x_1 - x_2 + 2x_3 &= 7 \\ 5x_1 + 3x_2 - 4x_3 &= 2 \end{aligned} \right\} \begin{array}{l} \text{3 equations, 3 variables} \end{array}$$

Although superficially it appears that $n = r$, such is not the case because the rank of the coefficient matrix is 2. Is the rank of the augmented matrix

$$\begin{bmatrix} 1 & 2 & -3 & 1 \\ 3 & -1 & 2 & 7 \\ 5 & 3 & -4 & 2 \end{bmatrix}$$

equal to 2 or to 3? The rank is 3, and thus there is no unique solution. This is really a case of $r < n$; one equation is not independent.

$r < n$ Multiple solutions exist.

Example 1:

$$\begin{aligned} x_1 + 2x_2 + x_3 &= 3 \\ 2x_1 + x_2 - x_3 &= 1 \end{aligned}$$

The rank of the coefficient matrix and the augmented matrix are both equal to 2, and $n = 3$. Multiple solutions exist.

Example 2

$$\left. \begin{array}{l} -2x_1 + 5x_2 + 7x_3 = 6 \\ -x_1 + x_2 + 2x_3 = 1 \\ x_1 + 2x_2 + x_3 = 3 \end{array} \right\} \text{3 equations, 3 variables}$$

The rank of the coefficient matrix is 2.

The rank of the augmented matrix is also 2. Thus, $r = 2$ and $n = 3$. Multiple solutions exist.

$$r > n$$

No solution exists.

Example 1:

$$\begin{array}{l} x_1 + 2x_2 = 4 \\ x_1 + 3x_2 = 1 \\ 2x_1 + 5x_2 = 3 \end{array} \quad \text{3 (inconsistent) equations, 2 variables}$$

The rank of the coefficient matrix = 2.

The rank of the augmented matrix = 3.

and no solution exists.

8. How to determine the number of independent components in the Gibbs phase rule

In Chapter 19, Equation (19.1), the phase rule was stated as

$$\mathcal{F} = 2 - \mathcal{P} + C$$

Where \mathcal{F} = number of degrees of freedom

\mathcal{P} = number of phases that exist at equilibrium

C = number of independent chemical species in the system

Without reaction in the system, the number of species is equal to C . With reaction in the system, the value for the number of species may have to be reduced because C is equal to the rank of the species matrix. For example, in Example 19.2, Part a, the number of species was 5: CO , CO_2 , H_2 , H_2O , and CH_4 . The species matrix is

	CO ₂	CO	H ₂	H ₂ O	CH ₄
C	1	1	0	0	1
H	0	0	2	2	4
O	1	2	0	1	0

The rank of the species matrix is 3, hence $C = 3$.

For Part b of Example 19.2, the number of species was 4. The species matrix is

	ZnO	C	CO	Zn
Zn	1	0	0	1
O	1	0	1	0
C	0	1	1	0

and the rank of the matrix is 3, hence $C = 3$.

L.2 Nonlinear Independent Equations

The precise criteria used to ascertain if a linear system of equations is determinate cannot be neatly extended to nonlinear systems of equations. Furthermore, the solution of sets of nonlinear equations requires the use of computer codes that may fail to solve your problem for one or more of a variety of reasons, a few of which are mentioned below. The problem to be solved can be written as

$$\left. \begin{aligned} f_1(x_1, \dots, x_n) &= 0 \\ f_2(x_1, \dots, x_n) &= 0 \\ &\dots \\ f_n(x_1, \dots, x_n) &= 0 \end{aligned} \right\} \mathbf{f}(\mathbf{x}) = \mathbf{0} \quad (\text{L.6})$$

where each function $f_i(x_1, \dots, x_n)$ corresponds to a nonlinear function containing one or more of the variables whose values are unknown.

Figure L.3 classifies the major general methods of solving systems of nonlinear equations. Within each category and as combinations of categories you can find innumerable variations and submethods in the literature and available as computer codes.

Newton's Method

Refer to Equation (L.6). For a single equation (and variable), $f(x) = 0$, Newton's method uses the expansion of $f(x)$ in a first-order Taylor series about a reference point (a starting guess for the solution) x_0 .

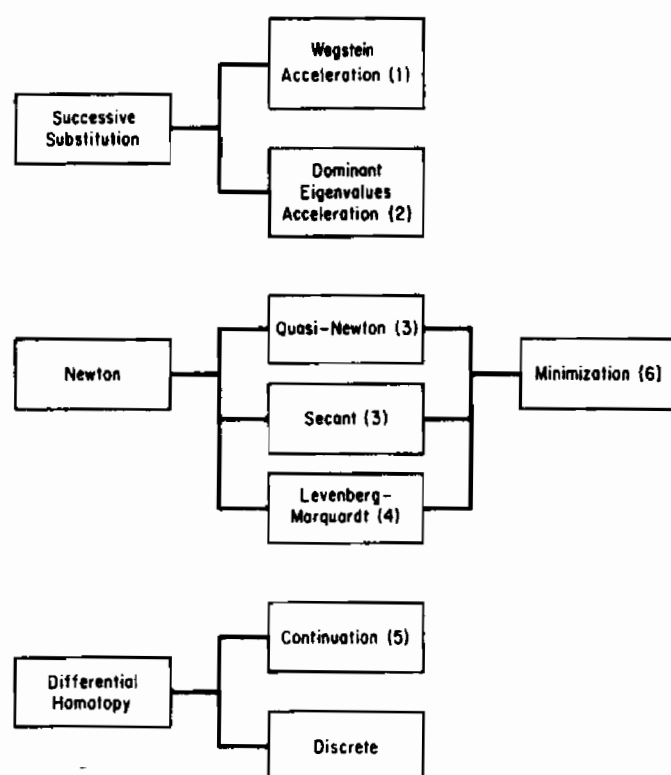


Figure L.3 General categories of techniques to solve nonlinear equations. From: 1. Wegstein, J. H. *Comm. ACM.*, 1, 9 (1958); 2. Orbach, O., and C. M. Crowe. *Can. J. Chem. Eng.*, 49, 509 (1971); 3. Dennis, J. E. and R. B. Schnabel. *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*. Englewood Cliffs, NJ, Prentice-Hall (1983); 4. Marquardt, D. *SIAM J Appl. Math.*, 11, 431 (1963); 5. Davidenko, D., *Ukrain Math.*, 5, 196 (1953); 6. Edgar, T. F., D. M. Himmelblau, and L. Lasdon. *Optimization of Chemical Processes* 2d ed. New York: McGraw-Hill (2002).

$$f(x) \simeq f(x_0) + \frac{df(x_0)}{dx}(x - x_0) \quad (\text{L.7})$$

Note that Equation (L.7) is a *linear equation* that is tangent to $f(x)$ at x_0 . Examine Figure L.4. The righthand side of Equation (L.7) is equated to zero and the resulting equation solved for $(x - x_0)$.

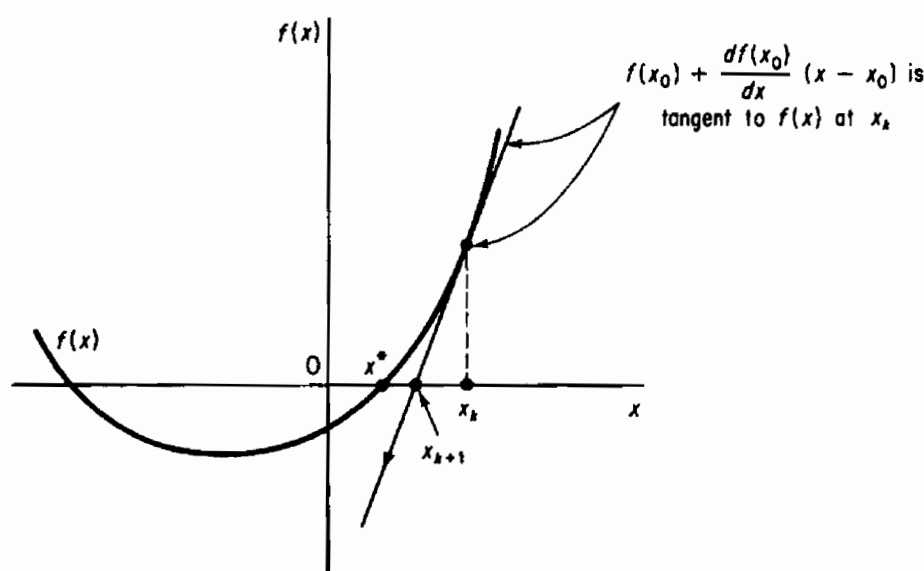


Figure L.4 Newton's method applied to the solution of $f(x) = 0$ starting at x_k ; x_{k+1} is the next reference point for linearization. x^* is the solution.

$$x - x_0 = -\frac{f(x_0)}{df(x_0)/dx} \quad (\text{L.8})$$

For example, suppose that $f(x) = 4x^3 - 1 = 0$, hence $df(x)/dx = 12x^2$. The sequence of steps to apply Newton's method using Equation (L.8) starting at $x_0 = 3$ would be

$$\begin{aligned} x_1 &= x_0 - \frac{4x^3 - 1}{12x^2} \\ &= 3 - \frac{107}{108} = 2.009259 \\ x_2 &= 2.00926 - \frac{31.4465}{48.4454} = 1.36015 \end{aligned}$$

Additional iterations yield the following values for x_k :

k	x_k
0	3.00000
1	2.009259
2	1.3601480
3	0.9518103
4	0.7265254
5	0.6422266
6	0.6301933
7	0.6299606
8	0.6299605
9	0.6299605

so that the solution is given with increasing precision as k increases.

Suppose that two independent equations in two variables whose values are to be determined are

$$\begin{aligned} f_1(x_1, x_2) &= 0 \\ f_2(x_1, x_2) &= 0 \end{aligned} \quad (\text{L.9})$$

To apply Newton's method, expand each equation as a first-order Taylor series to get a set of linear equations at the point (x_{10}, x_{20}) .

$$\begin{aligned} f_1(x_1, x_2) &\simeq f_1(x_{10}, x_{20}) + \frac{\partial f_1(x_{10}, x_{20})}{\partial x_1}(x_1 - x_{10}) + \frac{\partial f_1(x_{10}, x_{20})}{\partial x_2}(x_2 - x_{20}) \\ f_2(x_1, x_2) &\simeq f_2(x_{10}, x_{20}) + \frac{\partial f_2(x_{10}, x_{20})}{\partial x_1}(x_1 - x_{10}) + \frac{\partial f_2(x_{10}, x_{20})}{\partial x_2}(x_2 - x_{20}) \end{aligned} \quad (\text{L.10})$$

Let the partial derivatives be designed by the constants $a_{ij} = \partial f_i / \partial x_j$ to simplify the notation, and let $(x_i - x_{i0}) = \Delta x_i$. Then, after equating the righthand side of Equations (L.10) to zero, they become

$$\begin{aligned} a_{11} \Delta x_1 + a_{12} \Delta x_2 &= -f_1(x_{10}, x_{20}) \\ a_{21} \Delta x_1 + a_{22} \Delta x_2 &= -f_2(x_{10}, x_{20}) \end{aligned} \quad (\text{L.11})$$

These equations are linear and can be solved by a linear equation solver to get the next reference point (x_{11}, x_{21}) . Iteration is continued until a solution of satisfactory precision is reached. Of course, a solution may not be reached, as illustrated in Figure L.5c, or

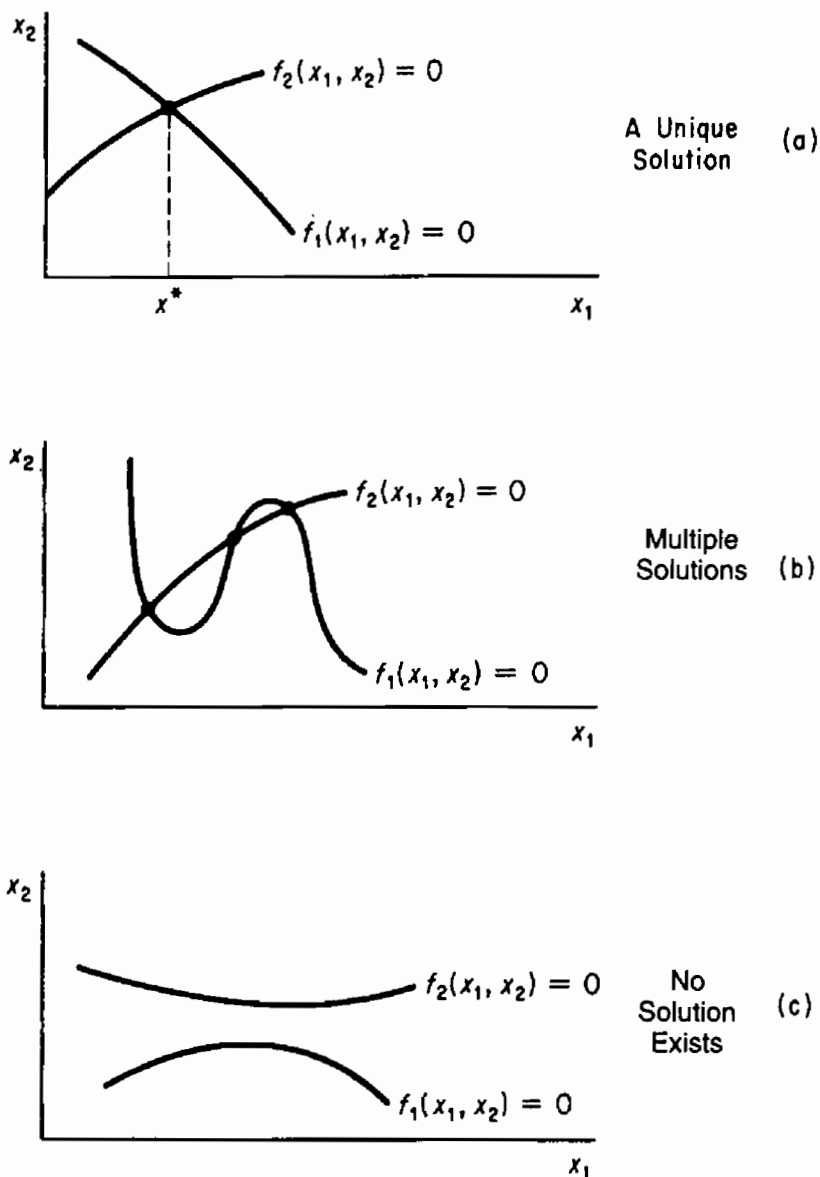


Figure L.5 Possible cases for the solution of two independent nonlinear equations $f_1(x_1, x_2) = 0$ and $f_2(x_1, x_2) = 0$ in two unknown variables.

may not be reached because of round-off or truncation errors. If the Jacobian matrix [see Equation (L.12) below] is singular, the linearized equations may have no solution or a whole family of solutions, and Newton's method probably will fail to obtain a solution. It is quite common for the Jacobian matrix to become ill-conditioned because if x_0 is far from the solution or the nonlinear equations are badly scaled, the correct solution will not be obtained.

The analog of (L.11) in matrix notation is

$$\mathbf{J}_k(\mathbf{x} - \mathbf{x}_k) = -\mathbf{f}(\mathbf{x}_k) \quad (\text{L.12})$$

where \mathbf{J} is the Jacobian matrix (the matrix whose elements are composed of the first partial derivatives of the equations with respect to the variables). For two equations

$$\mathbf{J} = \begin{bmatrix} \partial f_1(\mathbf{x})/\partial x_1 & \partial f_1(\mathbf{x})/\partial x_2 \\ \partial f_2(\mathbf{x})/\partial x_1 & \partial f_2(\mathbf{x})/\partial x_2 \end{bmatrix} \quad \mathbf{x} = \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \end{bmatrix} \quad \mathbf{f} = \begin{bmatrix} f_1 \\ f_2 \end{bmatrix}$$

Information concerning the other methods of solving nonlinear equations shown in Figure L.3 will be found on the CD that accompanies this book.

FITTING FUNCTIONS TO DATA

Frequently, you would like to estimate the best values of the coefficients in an equation from experimental data. The equation might be a theoretical law or just a polynomial, but the procedure is the same. Let y be the dependent variable in the equation, b_i be the coefficients in the equation, and x_i be the independent variables in the equation so that the model is of the form

$$y = f(b_0, b_1, \dots; x_0, x_1, \dots) \quad (\text{M.1})$$

Let ϵ represent the error between the observation of y , Y , and the predicted value of y using the values of x_i and the estimated values of the coefficients b_i :

$$Y = y + \epsilon \quad (\text{M.2})$$

The classical way to get the best estimates of the coefficients is by least squares, that is, by minimizing the sum of the squares of the errors (of the deviations) between Y and y for all the j sets of experimental data, $j = 1$ to p :

$$\text{Minimize } F = \sum_{j=1}^p (\epsilon_j)^2 = \sum_{j=1}^p (Y_j - f_j)^2 \quad (\text{M.3})$$

Let us use a model linear in the coefficients with one independent variable x

$$y = b_0 + b_1 x \quad (\text{M.4})$$

(in which x_0 associated with b_0 always equals 1 in order to have an intercept) to illustrate the principal features of the least-squares method to estimate the model coefficients. The objective function is

$$F = \sum_{j=1}^p (Y_j - y_j)^2 = \sum_{j=1}^p (Y_j - b_0 - b_1 x_j)^2 \quad (\text{M.5})$$

There are two unknown coefficients, b_0 and b_1 , and p known pairs of experimental values of Y_j and x_j . We want to minimize F with respect to b_0 and b_1 . Recall from calculus that you take the first partial derivatives of F and equate them to zero to get the necessary conditions for a minimum.

$$\frac{\partial F}{\partial b_0} = 0 = 2 \sum_{j=1}^p (Y_j - b_0 - b_1 x_j)(-1) \quad (\text{M.6a})$$

$$\frac{\partial F}{\partial b_1} = 0 = 2 \sum_{j=1}^p (Y_j - b_0 - b_1 x_j)(-x_j) \quad (\text{M.6b})$$

Rearrangement yields a set of linear equations in two unknowns, b_0 and b_1 :

$$\begin{aligned} \sum_{j=1}^p b_0 + \sum_{j=1}^p b_1 x_j &= \sum_{j=1}^p Y_j \\ \sum_{j=1}^p b_0 x_j + \sum_{j=1}^p b_1 x_j^2 &= \sum_{j=1}^p x_j Y_j \end{aligned}$$

The summation $\sum_{j=1}^p b_0$ is $(p)(b_0)$ and in the other summations the constants b_0 and b_1 can be removed from within the summation signs so that

$$b_0(p) + b_1 \sum_{j=1}^p x_j = \sum_{j=1}^p Y_j \quad (\text{M.7a})$$

$$b_0 \sum_{j=1}^p x_j + b_1 \sum_{j=1}^p x_j^2 = \sum_{j=1}^p x_j Y_j \quad (\text{M.7b})$$

The two linear equations above in two unknowns, b_0 and b_1 , can be solved quite easily for b_0 the intercept and b_1 the slope.

EXAMPLE M.1 Application of Least Squares

Fit the model $y = \beta_0 + \beta_1 x$ to the following data (Y is the measured response and x the independent variable).

x	Y
0	0
1	2
2	4
3	6
4	8
5	10

Solution

The computations needed to solve Equation (M.7) are

$$\sum x_j = 15 \quad \sum x_j Y_j = 110$$

$$\sum Y_j = 30 \quad \sum x_j^2 = 55$$

Then

$$6b_0 + 15b_1 = 30$$

$$15b_0 + 55b_1 = 110$$

Solution of these two equations yields

$$b_0 = 0 \quad b_1 = 2$$

and the model becomes $\hat{Y} = 2x$, where \hat{Y} is the predicted value for a given x .

The least-squares procedure outlined above can be extended to any number of variables as long as the model is linear in the coefficients. For example, a polynomial

$$y = a + bx + cx^2$$

is linear in the coefficients (but not in x), and would be represented as

$$y = b_0 + b_1x_1 + b_2x_2$$

where $a = b_0$, $b = b_1$, $c = b_2$, $x_1 = x$, and $x_2 = x^2$. Linear equations equivalent to Equation (M.7) with several independent variables can be solved via a computer. If the equation you want to fit is nonlinear in the coefficients, such as

$$y = b_0 e^{b_1 x} + b_2 x^2$$

you can minimize F in Equation (M.3) directly by the computer program on the disk in the back of this book, or by using a nonlinear least-squares computer code taken from a library of computer codes.

Additional useful information can be extracted from a least-squares analysis if four basic assumptions are made in addition to the presumed linearity of y in x :

1. The x 's are deterministic variables (not random).
2. The variance of ϵ_j is constant or varies only with the x 's.
3. The observations Y_j are mutually statistically independent.
4. The distribution of Y_j about y_j given x_j is a normal distribution.

For further details, see Box, Hunter, and Hunter¹ or Box and Draper.²

¹G. E. P. Box, W. G. Hunter, and J. S. Hunter. *Statistics for Experimenters*. New York: Wiley-Interscience (1978).

²G. E. P. Box and N. R. Draper. *Empirical Model Building and Response Surfaces*. New York: Wiley (1987).



APPENDIX N

ANSWERS TO SELECTED PROBLEMS

Chapter 1

- 1.1 (a) $4.17 \times 10^9 \text{ m}^3$; (b) 449 gal/min
- 1.4 (a) 88 ft/sec; (b) $3.52 \times 10^4 \text{ kg/m}^2$; (c) 4.79 nm/sec^2
- 1.5 (b) 4; (c) 1; (g) 1
- 1.8 112.5 min
- 1.11 $1.49 \times 10^4 \text{ kJ/(day)(m}^2\text{)(}^\circ\text{C/cm)}$
- 1.14 The object has a mass of 21.3 kg, and the force to support the mass (mg) corresponds to the weight.
- 1.17 11,200 (ft) (lb_f)
- 1.20 No. The g should be g_c
- 1.23 $u' = 2.57 \text{ k } (\tau'/e')$
- 1.26 0.943 has no associated units
- 1.30 Two
- 1.33 569.8 cm^2

Chapter 2

- 2.1 The first paragraph is OK. The second paragraph is wrong—molecular weight is not dimensionless.
- 2.4 All of the answers are wrong.
- 2.7 1. (d); 2 (c)
- 2.10 (a) 100.9 g/g mol CaCO_3 ; (c) 0.200 lb mol/lb CaCO_3
- 2.13 $\text{C}_{12}\text{O}_{11}\text{H}_{22}$
- 2.16 152 ft^3
- 2.19 (a) 1,100 g; (b) 1.9 kg polymer
- 2.22 59.29 lb/ft^3 ; 7.93 lb/gal
- 2.25 51 lb/ft^3
- 2.28 The answer, $3.90 \times 10^{-4} \text{ ppm}$, is just below the limit.
- 2.31 0.879

- 2.34 0.33 m
- 2.37 132 min
- 2.40 Na: 0.22, Cl: 0.33, O: 0.45
- 2.43 21.8 kg/kg mol
- 2.46 CO₂: 0.56; N₂: 0.44 (mole fractions)
- 2.49 19%
- 2.52 mass fraction H₂S = 2.70×10^{-4}

Chapter 3

- 3.1 (a) 100 or 1 g mol (use SI units); (d) use 1 or 100 mol (SI or AE)
- 3.3 134.2 lb Cl or 1 day (10.7×10^6 gal water)

Chapter 4

- 4.1 263K, 14°F, 474°R
- 4.4 (a) 50°F; (c) 241.3K
- 4.8 (a) 600°R, 333K, 60°C; (c) 40°F, 277.8K, 4.5°C
- 4.10 Yes, if the expansion is linear with temperature.

Chapter 5

- 5.1 (a) 15,000 kg; (b) 1.47 kPa (0.21 psi)
- 5.4 7.66 mm Hg
- 5.7 54.6 ft³/hr
- 5.10 Neither (the pressure varies continuously)
- 5.13 438 kPa
- 5.16 2.06 psia
- 5.19 66.7 kPa absolute
- 5.22 A (18.4 mm Hg difference)
- 5.26 210 in. H₂O
- 5.29 443 mm Hg (8.57 psia)
- 5.32 1.0 psig

Chapter 6

- 6.1 1200 kg
- 6.4 The balance on NaCl gives 4690 in \approx 4696 out, hence closure is good.

- 6.7 No ($In = 2.5 \times 10^6$, $out = 2.278 \times 10^6$)
6.10 System boundary includes both the pumps and soil at the end of the pipes.
6.12 (a) closed; (b) open; (c) open; (d) closed
6.16 (a) open, unsteady state; (b) open, unsteady state; (c) open, steady state
6.19 A reaction may occur in the system
6.22 (1): d, f; (2): a, e; (3): a, e (excluding vaporization) or d (with vaporization), f

Chapter 7

- 7.1 3 component plus 1 total; only 3 are independent
7.3 (a) No, and thus no solution; (b) independent but 2 solutions
7.5 (a) No
7.8 Examine the C_3H_8 row. No concentration reaches 50%.
7.11 The degrees of freedom equal 5. You can make any set of measurements that results in independent equations (assuming equal accuracy).
7.13 (d) unknowns: A, B, C; independent equations: 2 material balances plus 1 basis; (g) 1.40

Chapter 8

- 8.1 Yes
8.4 (a) Water = 5 mL, area = 141 mg; (b) 0.0934 mg/mL
8.7 26.5 lb
8.10 (a) $A = 0.600$, $B = 0.350$, $C = 0.05$; (b) an infinite number of choices
8.13 8.33×10^4 lb/hr
8.16 51.8 g $Na_2B_4O_7/100$ g H_2O
8.19 (a) $W = 23.34$ lb; (b) 66.5%
8.22 35 lb
8.25 (a) 0.64; (b) 655 g/min

Chapter 9

- 9.1 (a) 7.33 g $BaCl_2$; (e) 3.04 g Na_2SO_4 ; (h) 8.21 lb $BaSO_4$
9.4 (a) $a_1 = 3$, $a_2 = 4$, $a_3 = 28$, $a_4 = 28$, $a_5 = 6$, $a_6 = 9$
9.7 $BaI_2 \cdot 2H_2O$
9.10 (a) 2.08 lb; (b) 0.445 lb Cl_2 ; (c) 15,400 lb seawater; (d) 1.176 lb $C_2H_4Br_2$
9.13 12.4%
9.16 Very little, about 1.5%
9.19 Extent of reaction = 0.557; 1.341 g mol

- 9.22 (a) 145%; (b) 70.7%; (c) 0.205
9.25 0.619
9.27 (a) 33% excess C; (b) 86.0% Fe_2O_3 ; (c) 938 lb CO
9.30 (a) CO is limiting; (b) H_2O is excess; (c) 0.514; (f) 0.60 mol CO_2

Chapter 10

- 10.1 (a) 0.25, (b) 0.5
10.4 O and H balances not exact but close (difference perhaps caused by roundoff?).
10.7 20%
10.11 $\text{NH}_4\text{OH} = 232\text{g}$, $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 = 336.9\text{ g}$
10.13 CO_2 : 13.0%, H_2O : 14.3%, N_2 : 67.6%, O_2 : 5.1%
10.16 (a) 17%; (b) CH_4 : 89.8%, N_2 : 10.2%
10.18 22%
10.21 (a) 137.8 mol; (b) in percent values are CO_2 : 14.3, O_2 : 3.7, N_2 : 72.4, H_2O : 9.6
10.25 Yes. 0.236 mol air leaked /mol exhaust gas
10.28 (a) 92.2%; (b) 10.8%

Chapter 11

- 11.1 2
11.5 (a) Variables: In total 8 stream flows plus 19 mass fractions; unknowns: 6 stream flows plus 10 mass fractions; (b) independent material balances = 8. Note the independent specifications of sum of mass fractions = 8.
11.8 (a) $W = 500\text{ kg/hr}$, $D = 500\text{ kg/hr}$; (b) $A = 281\text{ kg/hr}$, $B = 719\text{ kg/hr}$, $C = 219\text{ kg/hr}$
11.11 Stream S^1 : $B_z = 0.97$, $X_y = 0.03$; Stream F^1 : $B_z = 0.082$, $X_y = 0.018$; Stream S^2 : $B_z = 0.82$, $X_y = 0.18$
11.14 241 kg
11.17 (a) 91.2%; (b) 0.44 lb Cl_2/lb product; (c) 1.22 lb H_2O

Chapter 12

- 12.1 (a) 1; (c) 0
12.4 The calculated values are not correct.
12.7 7670 kg/hr
12.10 (a) recycle rate = 57.2 gal/day; (b) mass fraction of oil plus dirt = 4.43×10^{-4}

- 12.13 (a) 719 kg/hr; (b) 1375 kg Benzene/hr at D and 1124 kg/hr at C both SO₂ free
12.16 (a) 111 kg (0.703 kg mol); (b) 760 kg
12.19 (a) 50 lb/hr; (b) 764 lb/hr
12.23 Recycle = 111 kg mol
12.26 By inspection you can see that the flow of Cl₂ and H₂ into the separator is going the wrong way.

Chapter 13

- 13.1 0.0944 lb H₂O
13.4 (a) Specific volume = 13.56 ft³/lb; (b) molal specific volume = 392.8 ft³/lb mol
13.6 51.9 psig
13.9 221 psig
13.12 41.4 m
13.15 2.99 ft diameter
13.18 (a) 0.047 ft³ SC; (b) 1.1×10^{-7} hr
13.22 10.6%
13.24 (c) 10.73; (d) 8.314
13.27 1.48
13.30 (a) 5.28%; (b) 30.3 lb/lb mol; (c) 1.045; (d) 0.190; (e) 7.54
13.34 (a) In mm Hg, CO₂: 148, O₂: 444, N₂: 148; (b) Yes, CO₂: 158, O₂: 474, N₂: 158
13.37 366 kPa
13.40 8.46×10^6 m³/min
13.44 0.284
13.47 (b) 575 mol C₄H₁₀/day; (a) 1,270 m³/day
13.50 (a) 3980 ft³/min; (b) 20,500 ft³/min

Chapter 14

- 14.1 (a) 141 atm; (b) 144 atm
14.4 1189°R (729°F)
14.7 0.608 lb
14.10 0.0127 m³/kg
14.12 102 cm³ (C₂H₅Cl is a *liquid* at the stated conditions)
14.15 (a) 4.167×10^{-4} lb mol/hr; (b) 0.98 hr; (c) 1.75×10^{-5} lb mol/ft³; (d) the CO alarms would sound a warning of a leak
14.18 0.29 (a decrease from 1.0)
14.21 2.88 ft³ (at 180°F and 2415 psia)
14.25 Select 1A because it is cheapest. Use 30 cylinders.

Chapter 15

- 15.2 e (assuming you have a handbook nearby)
15.5 RK: 2.126×10^3 kPa, SRK: 2.111×10^3 kPa (not a significant difference)
15.8 2460 psia
15.11 VdW: 10.6 g mol, RK: 10.6 g mol
15.14 266 kg
15.17 (a) VdW: 17.8 lb; (b) compressibility factor: 23.4 lb
15.19 1.01×10^4 kPa

Chapter 16

- 16.1 1:(1), 2:(2), 6:(1)
16.5 e
16.6 all true
16.10 (a) $p^* = 70.51$ mm Hg versus 70.55 from CD.
16.13 No. A typo occurred (equate the equations to get $T = 98.8^\circ\text{C}$)
16.16 $a = -1199.26$, $b = 532.27$, $c = -79.03$, $d = 3.9638$
16.19 (a) $0.837 \text{ m}^3/\text{kg}$, (d) $1.296 \text{ ft}^3/\text{lb}$
16.22 Mass liquid = 0.164 lb, Mass vapor = 1.818 lb, Volume liquid = 0.00288 ft^3 ,
Volume vapor = 9.952 ft^3
16.25 145 ft/s
16.28 ~ 3.3 atm

Chapter 17

- 17.1 (a) 104.8 kPa; (b) 0.0349
17.4 13.95 kg
17.7 9.62 lb H_2O
17.11 (a) -11.5°C (-15°C from the CD) at 1.4%; (b) 15.4°C for 8%
17.14 $1.93 \times 10^{-2} \text{ m}^3/\text{min}$ (at 100 kPa and 20°C)
17.17 5.4×10^{-4} psia (the Hg will not condense)
17.20 22 kg
17.23 104°F (40°C)
17.26 3940 ft^3 (at 800 mm Hg and 200°F)

Chapter 18

- 18.1 (a) 12.2%; (b) 14.9%; (c) 24°C
18.4 (a) 14.9%; (b) RH = 100% (condensation occurs) hence $T \cong 75^\circ\text{F}$

- 18.7 (a) Yes; (b) 53 ft³; (c) 0.17
18.10 941 kg
18.14 0.77
18.17 24,700 ft³/hr of dry air
18.20 2.00
18.23 0.137
18.26 0.48
18.28 (a) 0.20 mol; (b) 96.5 lb; (d) 232 lb H₂O

Chapter 19

- 19.1 2
19.4 (a) $P = 4$ (max), (b) $C = 3$
19.7 2
19.10 Yes (use plot or curve fitting program)
19.14 (a) mol fraction, Bz: 0.0316, Tol: 0.0126; (b) Yes
19.18 (a) 80.95 mm Hg (10.8 kPa); (b) mol fractions, P: 0.90, H: 0.10
19.21 (a) mol fraction in liquid $P = 0.56$; (b) mol fraction in vapor $P = 0.88$
19.24 $T = 413$ K
19.28 $T = 242$ K
19.31 Statements are OK, but to be precise the composition should be specified.

Chapter 20

- 20.1 (a) Freundlich: $k = 1.381$, $n = 0.197$; (b) fit is reasonably good
20.4 Let $C_{f_2} = 0$. Then $C_{s_1} = 1.06 C_{f_1}^{0.405}$
20.7 (b) 32.8 g mol BDA/min; (a) 0.0143

Chapter 21

- 21.1 (a) 2.5×10^4 cal/kg; (b) 1.048×10^5 J/kg; (c) 2.91×10^{-2} (kW)(h)/kg (d) 3.5×10^4 (ft)(lb_f)/(lb_m)
21.4 8.86×10^{-4} (G^{0.6})(J)/(D^{0.4})(min)(cm²)(°C)
21.8 Yes. In a short interval, energy/time can be large.
21.10 Yes
21.13 One-quarter hour of exercise uses 630 kJ; an insufficient time
21.17 a, b, c are intensive; d is extensive
21.20 -45.5 kJ
21.22 -3.16×10^5 (lb_f)(ft)

- 21.26 Heat is not conserved, it is transferred. The transfer from one system equals the transfer into another system, but this is not conservation.
- 21.29 (a) F, (b) F, (c) T, (d) F, (e) T, (f) T but debatable, (g) F, (h) F
- 21.32 1.55 (ft)(lb_f)
- 21.35 2940J
- 21.38 624J
- 21.42 ΔH and ΔU are zero because they are state variables.
- 21.45 (a) $V = 36.5 \text{ ft}^3$ at 100 atm and 40°F, $p = 180 \text{ atm}$; (c) $\Delta H = 32,000 \text{ Btu}$; (b) $\Delta U = 1215 + 31.5 T(^{\circ}\text{C})$
- 21.48 (a) F, (b) F, (c) F, (d) T

Chapter 22

- 22.1 All of them
- 22.3 (a) System: can plus liquid so $Q = 0$, $W \neq 0$; (b) system: motor so $Q = 0$, $W \neq 0$ but may get hot; (c) system: pipe plus water so $Q = 0$, $W \neq 0$.
- 22.6 $Q = 807.3 \text{ Btu/lb}$, $W = 0$, $\Delta H = 889 \text{ Btu/lb}$, $\Delta U = 807 \text{ Btu/lb}$
- 22.9 Final $T = 45^{\circ}\text{C} > 30^{\circ}\text{C}$
- 22.12 (a) $W = 0$; (b) and (c) $\Delta U = 0.105 \text{ Btu} = Q$; (d) 10.7 ft^3
- 22.14 $Q = 28.8 \text{ Btu/lb}$, $W = 0$, $\Delta H = 38 \text{ Btu/lb}$, $\Delta U = 28.8 \text{ Btu/lb}$
- 22.17 $\dot{W} = 0.57 \text{ kW}$
- 22.20 (a) $Q = 970 \text{ Btu}$, $W = -72.8 \text{ Btu}$, $\Delta U = 897 \text{ Btu}$, $\Delta H = 970.0 \text{ Btu}$; (b) $Q = 970 \text{ Btu}$, $W = 0$, $\Delta U = -180 \text{ Btu}$, $\Delta H = 1150.3 \text{ Btu}$
- 22.23 $T \cong 39^{\circ}\text{F}$
- 22.26 0.61 kW
- 22.29 $Q = -4.1 \times 10^4 \text{ Btu}$, hence not adiabatic
- 22.32 $T = 21.9^{\circ}\text{C}$

Chapter 23

- 23.2 Latent heat refers to energy in a phase change. Sensible heat refers to energy changes for a single phase between phase transitions.
- 23.5 (a) 1, (b) 3, (c) 5, (d) 2, (e) 4. Boiling is at 4 by extending the scale to the left. Freezing is at 1 to the left by extending the scale
- 23.8 $\Delta H_v = 58,070 \text{ J/g mol}$
- 23.11 $\Delta H_v \cong 30.6 \text{ kJ/g mol}$
- 23.14 The data are not consistent because $(dp/dT) > (\Delta \hat{H}_v)/(T)(\Delta V)$.
- 23.17 (a) $C_p = 34.586 + 0.0357T - 7.996 \times 10^{-6} T^2$;
(b) $C_p = 34.826 + 0.03265T - 1.45 \times 10^{-6} T^2 - 3.636 \times 10^{-9} T^3$
- 23.21 $C_p = 0.226 + 3.118 \times 10^{-5} T_{\text{°F}} - 2.765 \times 10^{-9} T_{\text{°F}}^2$

- 23.24 $C_p = 92.38 + 3.754 \times 10^{-2}T - (2.186 \times 10^6/T^2)$
23.27 11,910 J
23.30 2.563×10^3 J/g mol or 2.580×10^3 J/g mol from the CD
23.33 -325,000 kJ
23.36 $\Delta H = -12,470$ kJ, $\Delta U = -9050$ kJ
23.38 (a) 3576 Btu; (b) 3576 Btu; (c) 1173.4 Btu; (d) 182 Btu/lb; (e) -964.2 Btu/lb
23.40 0.162
23.43 0.98
23.46 Yes, the reference state is arbitrary.
23.49 (1) 1956 J/g mol, (2) ~2040 J/g mol, (3) 1957 J/g mol; the CD gives 2038 J/g mol

Chapter 24

- 24.3 6
24.6 (a) (1) ignore PE , $\Delta PE = 0$; (2) $\Delta KE \cong 0$; (3) no reaction; (4) $W = 0$; (5) $\Delta E = 0$ (steady state), hence $\Delta H = Q$
(b) (1) ignore PE , $\Delta PE = 0$; (2) No reaction; (3) $W = 0$; (4) $\Delta E = 0$ (steady state); (5) $Q = 0$, hence $\Delta H + \Delta KE = 0$
24.9 -27.86 kJ/kg CO_2 (removed)
24.12 $Q = 0$, $W = 0$, $\Delta U = 0$
24.15 All value are Btu/lb. Step 1: $\Delta U = 2.5$, $\Delta H = 3.5$, $Q = ?$, $W = ?$; Step 2: $\Delta U = -73.8$, $\Delta H = -93.4$, $Q = -73.8$, $W = 0$; Step 3: $\Delta U = 71.3$, $\Delta H = 93.4$, $Q = 0$, $W = 71.3$
24.19 5.84 kW
24.22 -41.7 kW
24.25 (a) -17 Btu/lb; (b) 38°F; (c) -40 Btu/lb
24.28 22.1 lb steam
24.31 0.43
24.34 8.01×10^6 kJ
24.37 82.9 hp
24.39 (a) 8,422 lb/hr; (b) 46,580 lb/hr; (c) 182 hp; (d) 136 kW; (e) \$59,360/year

Chapter 25

- 25.1 2, 4, 6
25.4 20.1 kJ/g mol
25.8 -10,030 J/g mol C_3H_8
25.11 -4728 kJ/kg FeS_2
25.14 5×10^7 J/g mol G converted
25.17 (a) 113% larger; (b) 59% larger
25.20 15,980 Btu/lb mol

- 25.24 Yes
25.27 263 kJ/g mol
25.30 (a) 1.44×10^5 J/g mol C_6H_{12} ; (b) 1.68×10^5 J/g mol C_6H_{12}
25.33 -16,740 kJ (leaving)
25.36 -286.64 kJ/g mol H_2
25.39 -286.26 kJ
25.41 HHV = 2.11×10^5 kJ/m³

Chapter 26

- 26.1 \$1523 saved. Maintenance problems on shutting down and starting up.
26.4 (a) reduces, (b) increases, (c) reduces
26.7 2,320 lb/hr
26.11 90 ft³/min
26.14 2158 K
26.17 277%
26.20 $T \cong 3045$ K; $p = 962$ kPa (assuming ideal gas is probably OK)
26.23 -147.23 kJ/g mol CH_3OH (removed)
26.26 Savings = \$27,800/year
26.29 32.52 kJ/g mol on basis of $F = 100$ g mol

Chapter 27

- 27.1 (a) -3.76×10^4 J/kg
27.4 (a) $W = 0$; (b) -1312 Btu/lb mol
27.7 82%
27.9 82%
27.13 72.8 hp
27.16 $E_v = 81.8 + W$. If $W = 2.1$ (ft)(lb_f) on the water, the calculation is OK.
27.19 346 kg/s

Chapter 28

- 28.1 -441.62 kJ/g mol Li
28.4 (b) -3,390 J (absorbed)
28.7 (a) $T = 117^\circ C$; (b) 43 to 44% H_2SO_4 ; (c) 350 lb total, 335 lb liquid plus 15 lb of steam in the vapor phase
28.10 (c) 165°F
28.13 28%

Chapter 29

29.1 (a) $\cong 10^\circ\text{C}$; (b) 38%; (c) 0.79 kg H_2O /kg air

29.4 (a) 0.116 g A/g C; (b) 55.9%; (c) 1.22 J/(K)(g C); (d) 0.877 $\text{m}^3/\text{kg C}$; (e) 0.878 $\text{m}^3/\text{kg C}$

29.8 At 100% relative humidity (saturated air)

29.12 (a) 27°C , (b) 57%



NOMENCLATURE

- A = area
- A = constant
- a, b, c , and d = stoichiometric coefficients, for the species A, B, C , and D , respectively
- a = acceleration
- \mathbf{A} = coefficient matrix
- a = coefficient in general
- a = constant in van der Waal's equation (see table 15.1)
- a, b, c = constants in heat capacity equation
- $^{\circ}\text{API}$ = specific gravity of oil
- B = constant
- b = constant in van der Waals' equation (see table 15.1)
- B = rate of energy transfer accompanying w (mass transfer)
- (c) = crystalline
- C = constant in Eq. (1.1)
- C = number of chemical components in the phase rule
- $^{\circ}\text{C}$ = Celsius
- C_p = heat capacity at constant pressure
- C_s = humid heat
- C_v = heat capacity at constant volume
- D = diameter
- D = distillate product
- d = depth
- ds = displacement
- E = the rank of the component matrix
- E = total energy in system = $U + K + P$
- E_v = irreversible conversion of mechanical energy to internal energy
- f_{OA} = overall conversion
- f_{SP} = single pass conversion
- \mathbf{F} = force
- \mathcal{F} = number of degrees of freedom in the phase rule
- F = feed stream
- F = volumetric flow rate
- $^{\circ}\text{F}$ = Fahrenheit
- (g) = gas
- g = acceleration due to gravity
- g_c = conversion factor of $\frac{32.174(\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)}$
- G = rate of flow of suspension, lb/hr
- \hat{H} = enthalpy per unit mass or mole
- h = distance above reference plane
- H = enthalpy, with appropriate subscripts, relative to a reference enthalpy

\mathcal{H}	=	humidity, lb water vapor/lb dry air
(l)	=	liquid
h_c	=	heat transfer coefficient
H_i	=	Henry's law constant
$\Delta \hat{H}$	=	enthalpy change per unit mass or mole
ΔH	=	enthalpy change, with appropriate subscripts
ΔH_{rxn}	=	heat of reaction
ΔH_{soln}	=	heat of solution
ΔH_v	=	heat of vaporization
ΔH_c^0	=	standard heat of combustion
ΔH_f^0	=	standard heat of formation
$\Delta \hat{H}_v$	=	molar heat of vaporization
K	=	petroleum characterization factor
K	=	degree Kelvin
KE	=	kinetic energy
K_i	=	vapor/liquid equilibrium coefficient
L	=	moles of liquid
l	=	distance
lb	=	pound, as a mass (without subscript)
lb _f	=	pound, as a force
lb _m	=	pound, as a mass
m	=	mass of material
\dot{m}	=	number of equations
\dot{m}	=	rate of evaporation
m	=	mass transport through defined surfaces
m_A	=	mass flow of component A
mol. wt.	=	molecular weight (MW)
M	=	molar flow rate
M	=	number of input streams
n	=	number of moles
n	=	number of unknown variables
n_i	=	moles of species i present in the system after the reaction occurs
n_{i0}	=	moles of species i present in the system when the reaction starts
N	=	Avogadro's number (6.02×10^{23})
N_d	=	degrees of freedom
N_e	=	number of independent equations
N_{Re}	=	Reynolds number
N_S	=	number of streams
N_{SP}	=	number of chemical species
N_r	=	number of independent constraints
N	=	number of chemical species
N	=	number of output streams
N_v	=	total number of variables
o	=	output stream

\mathcal{P}	=	number of phases in the phase rule
p	=	partial pressure (with a suitable subscript for p)
p	=	pressure
p'_c	=	pseudocritical pressure
p^*	=	vapor pressure
p_c	=	critical pressure
PE	=	potential energy
P	=	product
p_0	=	pressure at the top of the column of fluid
p'_c	=	pseudoreduced pressure
p_r	=	reduced pressure = p/p_c
p_t	=	total pressure in a system
Q	=	heat transferred
\dot{Q}	=	rate of heat transferred (per unit time)
\hat{Q}	=	heat transfer/unit mass
q	=	volumetric flow rate
(s)	=	solid
R	=	total number of reactions.
R	=	recycle stream
R	=	universal gas constant
r	=	rank of a matrix
r_A	=	rate of generation or consumption of component A (by chemical reaction)
R	=	the size of the minimal set of reaction equations, i.e., the number of independent reactions
R	=	radius
r	=	distance from the axis
r^*	=	dimensionless variable
\mathcal{RH}	=	relative humidity
\mathcal{RS}	=	relative saturation
$^{\circ}\text{R}$	=	degree Rankine
S	=	the number of species involved in the process
S	=	cross-sectional area perpendicular to material flow
s	=	second
\mathbf{s}	=	pathway vector
sp gr	=	specific gravity
T	=	absolute temperature or temperature in general
t	=	time
T'_c	=	pseudocritical temperature
T'_r	=	pseudoreduced temperature
T_b	=	normal boiling point
T_c	=	critical temperature (absolute)
T_{DB}	=	dry-bulb temperature
T_f	=	melting point
T_r	=	reduced temperature = T/T_c

T_S	=	saturated equilibrium temperature of water
T_{WB}	=	wet-bulb temperature
U	=	internal energy
\hat{U}	=	internal energy per unit mass
V	=	humid volume per unit mass or mole)
\hat{V}	=	specific volume (volume per unit mass or mole)
V	=	system volume of fluid volume in general
v	=	velocity
ν	=	matrix of stoichiometric coefficients
ν_i	=	coefficient for species i in the chemical equation when written so that the sum of the terms equals zero.
\dot{V}	=	volumetric flow rate
V_c	=	critical volume
V_{ci}	=	ideal critical volume = RT_c/p_c
V_{ci}	=	psuedocritical ideal volume
V_g	=	volume of gas
V_l	=	volume of liquid
V_r	=	reduced volume = V/V_c
V_{ri}	=	ideal reduced volume = V/V_{ci}
\dot{W}	=	rate of work done by system (per unit time)
W	=	waste stream
W	=	work done by or on the system
w_A, w	=	rate of mass flow of component A and total mass flow, respectively, through system boundary other than a defined surface
x	=	mass or mole fraction in general
x	=	fractional quality
x	=	mass or mole fraction in the liquid phase for two-phase systems
x	=	unknown variable
y	=	cumulative mass of solute or gas adsorbed (adsorbate) per mass of adsorbent in the solid phase
y	=	mass or mole fraction in the vapor phase for two-phase systems
z	=	compressibility factor
z_c	=	critical compressibility factor
z_j	=	mole fraction of j

Greek letters:

$\alpha, \beta, \gamma, \sigma, \eta, \kappa$	=	constants
Δ	=	difference between exit and entering stream; also used for final minus initial in time, or small time increments
ρ	=	density
ρ_A, ρ	=	mass of component A, or total mass, respectively, per unit volume
ρ_B	=	bulk density
ρ_L	=	liquid

μ	=	viscosity
ε	=	error
ρ_v	=	vapor density
ω	=	Pitzer ascetric factor
ω	=	mass fraction
θ	=	time, or dimensionless time
λ	=	constant in equations of state
ξ	=	extent of reaction
ϕ	=	dimensionless temperature

Subscripts:

A, B	=	components in a mixture
c	=	critical
i	=	any component
i	=	ideal state
r	=	reduced state
t	=	total
1,2	=	system boundaries

Overlays:

\wedge	=	per unit mass or per mole
\cdot	=	per unit time (a rate)

INDEX

In this index the page numbers in *italic* refer to pages in Chapters 30–31 that will be found on the CD that accompanies this book. Pages in the problem Workbook are indexed separately, and that index will be found in the Workbook itself as well as proceeding this index.

Abbreviations

American Engineering, table, 9
SI prefixes, 10
SI tables, 9
Absolute error, 25
Absolute pressure, 103ff, 107, 402
Absolute temperature, 90, 402
Acceleration, 9, 17
Acentric factor, 446ff (*see also* Pitzer
acentric factor and CD)
table, 446
Accumulation, 135, 141
Addition of units, 12
Adiabatic, 610, 619
Adiabatic cooling line, 889
Adiabatic process, 619
Adiabatic reaction (combustion, flame)
temperature, 807
Adiabatic system, 40, 619ff
Adsorbate, 591
Adsorbent, 591

Adsorption, 591ff
Adsorption isotherms, 591ff
Air
average molecular weight, 59
composition, table, 60
excess, 285
required, 284
Air quality standards, 552
Alternative additions to gasoline, 77, 97,
768, 769, 784, 791, 797, 800
Alternative fuels, 504, 558
Alternative process evaluation, 65, 777, 789
American Engineering Units (AE), 7, 9, 404
Analysis of waste, table, 60
Answers to selected problems, Appendix N,
1089ff
Answers to self-assessment tests, Appendix
A, 997ff
Antoine Equation, 486
API, 53 (*see also* CD)
Atomic weight, 60

- Atomic weights and numbers, Appendix B, 1030ff
- Atmospheric pressure, 107
- Average molecular weight, 60ff, 78
- Azeotrope, 570
- Balancing a reaction equation**, 228
- Barometric pressure, 104, 107
- Basis, 78ff, 173
- Batch distillation, 980
- Batch process, 151ff
- Baume, 53
- Benedict-Webb-Rubin equation of state, 461
- Benzene-toluene phase diagram, 569–570
- Bernoulli equation, 850
- Biological materials, 20
- Biological systems, 33, 40, 41, 58, 77, 81, 536, 776, 800, 819, 835
- Bioventing soil, 162
- BLEVE explosion, 485, 689
- Block diagram, 306
- Boiling, 478
- Boundary, 609
- Bourdon gauge, 104
- Bubble point, 478, 575
- Bubblepoint temperature, 478
- Butane chart, 703
- Bypass stream, 365
- Calcination**, 986
- Calories, dietary, 611–612
- Carbon dioxide experiments, 437
- Carbon dioxide *p-H* chart, 1066 (*see also* CD)
- Catalyst regeneration, 344
- Cell growth, 33, 40, 41, 58, 77, 81, 536, 776, 800, 819, 835
- Celsius (°C), 90
- Centrifuge, 147
- Changing bases, 83ff
- Charts
 - butane, 703
 - carbon dioxide, 1066 (*see also* CD)
 - toluene, 1065 (*see also* CD)
- Check solution (*see* Validation)
- Chemical reactions, 149
- Chemisorption, 591
- Chen's equation, 685
- Clapeyron equation, 684
- Clausius-Clapeyron equation, 684
- Closed system, 136ff, 609
 - energy balance, 728
- Closed system, 609
- Closure, material balance, 375
- Coal, 84, 87
- Coal gasification, 714
- Coefficient of performance (COP), 844
- Cogeneration, 847
- Combustion, 283
 - complete, 284, 285
 - pollutants, 284
 - temperature, 807
- Combustion temperature, 807
- Complete combustion, 284, 285
- Component material balance, 145ff
- Components, 915
- Composition, 59ff
- Compound, 44
- Compressed liquid, 487
- Compressibility, 438ff
- Compressibility charts, 440ff (*see also* CD)
- Compressibility charts (*see* CD)
- Compressibility factor, 440, 445
- Computer data bases, 705
- Concentration, 62ff
- Condensation, 479–480, 514ff
 - cycle, 516
 - heat of, 682
 - material balances with, 522
 - of water from air, 547
 - temperature (*see* Dewpoint)
- Connections, 310
- Conservation of energy, 646ff
- Conservation of mass, 134
- Consumption, 150
- Contact process, 806
- Continuous process, 138

- Conversion, 18, 240ff, 314, 356, 357
 - g, , 18
 - factors, 18
 - of temperature, 92
 - of units, 14, 17
 - tables of factors (*see* inside front cover)
- Cooling, 515
- Cooling towers, 900
- Corresponding states, 436ff
- Cox chart, 493
- Cracking, 161
- Critical state (point), 436ff
- Critical properties, Appendix D (*see also* CD and the individual property)
- Cubic equations of state, 463
- Dalton's Law**, 413
- Deflagration, 125
- Degree of completion, 240ff
- Degree of freedom analysis, 178, 313, 913
 - analysis for an energy balance, 725
 - combined units, 925
 - example, 916ff
 - for combustion, 804
 - heat exchanger, 918
 - in the phase rule, 562
 - mixer, 918
 - splitter, 917
 - two phase equilibria, 919
 - with reaction, 803ff, 912ff
- Degrees of superheat (*see* superheated vapor)
- Dehydration, 544 (*see also* condensation)
- Density, 48ff
- Density of a gas, 408
 - alcohol water, figure, 50
 - of gas, 40
 - of water, figure, 48
- Dependent equations, 175
- Derived units, 7ff
- Dew point, 478, 510, 573
 - Calculation of, 511, 539
 - of binary mixture, 573
 - temperature, 510, 573, 889, 891
- Differential material balance, 142
- Differential pressure measurement, 104ff
- Dimensional consistency, 21ff
- Division of units, 12
- Dimensionless group, 22
- Dimensions, 6ff
- Distillation column, 159
- Distillation, 566, 742, 760
- Distribution coefficient, 570
- DNA, 29
- Draining tank, 977
- Dry basis, 284
- Dry bulb temperature, 886
- Drying, 207
- Dulong formula for HHV, 787
- Efficiency**, 843ff
- Efficiency, general, 844
 - calculation of, 845
 - of energy conversion, table 818, 844
 - plant, 845
- Electric work, 615
- Element material balances, 278, 1074ff
- Endothermic reaction, 765
- Energy 613ff (*see also* specific types)
 - definition, 614
 - from tides, 642
 - solar, 638
 - terminology, 608ff
 - transfer, 614
 - types, 613ff
 - units, 611
 - usage, 64
- Energy balances, 646ff
 - calculations using, 717ff
 - closed steady-state, 655ff, 725ff
 - closed unsteady-state, 648ff, 728ff
 - degrees of freedom, 603, 725
 - general without reaction, 658ff, 664
 - mechanical energy balance, 850
 - open steady-state, 666ff, 735ff
 - open unsteady-state, 657ff, 735ff
 - with reaction, 763ff, 802, 806
 - simplifications, 718ff
 - strategy in solving, 723

- Energy usage, 604
- Enthalpies of gases, tables, 1044ff
- Enthalpy, 631ff
 - calculation of changes in, 632, 681ff, 693
 - charts, 699ff, 1060ff (*see also* CD)
 - compressed liquids, 700
 - gas mixtures, 695
 - in steam tables, 701
 - phase transitions, 633
 - tables 699ff, 1059
- Enthalpy balance, 719 (*see also* Energy balance)
- Enthalpy-concentration charts
 - charts, 874ff, 1060ff (*see also* CD)
 - data, Appendix I, 1059ff
 - tables, 1059
- Environmental systems, 63, 517, 519, 789
- Equation-oriented method, 942
- Equations (*see also* material balances)
 - independent, 173, 174, 175, 304, 309, 914, 1069ff
 - linear, 1069
 - nonlinear, 180ff, 1080ff
 - reaction, 269
 - solution of, 1072ff, 1078ff
 - solution of cubic, 463ff
- Equations of state (EOS), 439, 460, table 461
- Equilibrium, 478
- Equilibrium ratio, 570 (*see also* K value)
- Equilibrium state, 609
- Equipment sketches, 55
- Equipment (*see* CD files and Problem Workbook on CD)
- Errors in numbers, 24
- Evaporation, 478 (*see also* Vaporization)
 - work in, 838
- Exactly specified, 178
- Excess air (or oxygen), 285
- Excess reactant, 237ff
- Exothermic reaction, 765
- Extensive property, 561
- Extent of reaction, 233ff, 262–264
- Extrapolation, 494
- Fahrenheit (°F)**, 90
- Feet of water, 101
- Final condition, 135, 141
- Fitting data, Appendix M, 1085ff
- Flame temperature, 807
- Flash, 575, 577
- Flow chart, 306
- Flow rate, 56
- Flow system, 137, 609 (*see also* open system)
- Flow work, 615, 659
- Flowsheet, 938
- Flowsheeting, 938
- Flowsheeting codes, 938ff
- Flue gas, 284
- Fluid flow relations, 36, 37, 38, 40, 56, 123
- Fluidized bed, 826
- Fluidized cracking, 344
- Force, 17
- Freezing, 478
- Fresh feed, 347
- Freundlich isotherm, 592
- Fuel cells 451, 713, 829
- Fundamental units, 7
- Fusion, 491
- g.**, 18
- Gardia, 499
- Gas mixtures, 412, 446, 467
- Gas, 398, 476
 - density, 408
- Gasoline blending, 579
- Gasoline, limits on components, 581
- Gauge pressure, 103
- Gauss-Jordan method of solving equations, 1072ff
- Generalized compressibility chart, 440ff
- General energy balance, 649ff, 658ff, 664
 - simplification, 718ff
- Generalized equation of state, 439
- Generation, 150
- Gibb's Phase Rule, 561ff
 - components in, 562, 1079
- Global warming, 623
- Gram mole, 43

- Gravity, 18
- Gross feed, 347–348
- Gross product, 348
- Group contribution method, 467
- H/C ratio for fuels**, 294
- Head of liquid, 102
- Heat (Q), 619ff
 - engine, 621
 - engine efficiency, 844
 - exchanger, 918
 - in the energy balance, 872
 - of combustion, 765ff (*see* Standard heat of combustion)
 - of condensation, 682
 - of dissolution, 865
 - of formation, table Appendix F, 1052ff (*see also* Standard heat of formation)
 - of fusion, 682
 - of mixing, 865ff
 - of reaction, 769ff
 - of solution and dilution, 865ff, Appendix H, 1058
 - of solution for HCl, table, 867
 - of solution at infinite dilution, 865
 - of solidification, 682
 - of sublimation, 682
 - of vaporization, 682
- Heat capacity, 628, 690
 - at constant pressure, 631
 - at constant volume, 628
 - average for mixtures, 692
 - conversion of units, 93, 693
 - empirical, 633
 - equation, conversion of, 93
 - equations for, 690ff
 - fitting to data, 694
 - ideal gas, table, 691
 - of combustion gases, figure, 691
- Heat capacity equations, table Appendix E, 1048ff
- Heat transfer (*see* Heat)
- Heat transfer coefficient, 38, 159, 637
- Heating value of coal, 786, 788
- Henry's law, 567
- Higher (gross) heating value (HHV), 786
- Holborn equation, 461
- Homogeneity of equations, 21
- Humid heat, 885
- Humid volume, 886
- Humidification of air, 545
- Humidifiers, 897
- Humidity, 538, 540
- Humidity chart, 888
 - application of, 892–893, 897
- Hydroforming, 756
- Hydrogen as a fuel, 825
- Hydrogen, pseudocritical parameters, 440ff
- Ideal critical volume**, 441, 449
- Ideal gas, 402ff
 - heat capacities, table, 691
 - law, 402
 - law, assumptions underlying, 403
 - material balances using, 416ff
 - mixture, 412
- Ideal gas constant, 405 (*see also* list inside front cover)
- Ideal process, 837
- Ideal reduced volume, 441
- Ideal reversible process, 837
- Ideal solution, 566, 865
- Implicit equation, 180
- Inches of mercury, 101
- Inches of water, 101
- Incremental (differential) heat of solution, 865
- Independent equations, 173, 174, 175, 308, 309, 914, 1069ff
 - element balances, 1074
 - nonlinear, 1080
 - reaction equations, 1075
 - solution of, 1076
- Independent material balance, 309, 313
- Independent reaction equations, 269, 1075
- Industrial applications of material balances, 373
- Initial condition, 135, 141, 974

- Input, 135
- Integral heat of solution, 865
- Integrated quantities, 613, 620
- Integrated material balances, 629
- Intensive property, 561
- Internal energy (U), 627ff
 - calculation of changes in, 629
- Interpolation, 491
 - in the steam tables, 491
- Interval, time, 141
- Invariant, 563
- Irreversible process, 837ff
- Isobaric, 610, 720
- Isochoric, 608, 610, 720
- Isometric, 720
- Isothermal, 610, 720

- joule, 9**

- K value, 570**
 - charts, 573
 - estimation of, 572
- Kammerlingh-Onnes equation, 461
- Kay's method, 446ff
- kilvin (K), 90
- Kilograms force, 101
- Kinetic energy (KE), 624
- Knowns, 178ff, 311

- Langmuir isotherm, 593**
- Latent heat, 682
- Law of corresponding states, 436
- Leaking tanks, 120
- Leaks, 863
- Least squares, 1085
- Length, 9–11
- Limiting reactant, 237ff, 264
- Linear equation, 180ff, 1080ff
- Liquid, 398
- Liquid head, 102
- Lost work (E_r), 850
- Lower (net) heating value (LHV), 786
- Lower explosive limit (LEL), 534
- Lower flammability limit (LFL), 587

- Manometer, 103**
- Mass, 17
- Mass flow rate, 53
- Mass fraction, 57ff
 - summation, 178
- Material balance, 129ff, 134, 261
 - closure, 375
 - combustion, 282
 - component, 145ff
 - differential, 143, 972ff
 - element, 278
 - ideal gas, 416
 - independent, 174ff, 308ff
 - industrial applications, 373
 - integrated, 142
 - linear, 180
 - multiple units, 332ff
 - nonlinear, 180ff, 1080ff
 - overall, 308ff
 - species, 261
 - unsteady-state, 972ff
 - total, 147
 - with adsorption, 596
 - with condensation, 522
 - with multiple reactions, 269
 - with partial saturation, 544ff
 - with reaction, 150, 261ff
- Mechanical efficiency, 844
- Mechanical energy, 848
- Mechanical energy balance, 850
- Mechanical work, 614
- Melting, 479
- Melting curve, 479
- Microelectronics, 22, 730
- Millimeters of mercury, 101
- Minimal set of reactions, 264, 1075ff
- Mixer, 50, 306, 918
- Modular method in flowsheeting, 942
- Molal saturation, 540
- Molality, 62
- Molar flow rate, 56
- Mole, 43ff

- Mole fraction, 57ff
 - summation of, 178
- Molecular weight, 43, 45
- Multiple units, 342ff
- Nanoparticles**, 469
- Nanotechnology, 17, 82, 109, 241
- Natural gas, units of pressure, 404
- Negative accumulation, 140
- Net product, 347
- Newton method of solving equations, 1080ff
- Nomenclature, 1100
- Nonlinear equation, 180ff, 1080ff
- Noncondensable gas, 476
- Non-dimensional group, 22
- Non-ideal vapor-liquid equilibria, 571
- Nonflow system, 609 (*see also* Closed system)
- Normal boiling point, 479
- Normal melting point, 479
- Normality, 62
- Nutrition labeling, 611
- Nutrition, 800
- Once-through fraction conversion**, 356
- Open equation form, 374
- Open system, 136ff, 609 (*see also* material and energy balances)
- Operations with units, 12
- Orifice, figure, 115
- Orsat analysis, 284
- Oscillating reactions, 982
- Output, 135
- Overall fraction conversion, 238, 356–357
- Overall material balance, 308
- Overall process, 310
- Overall product, 347
- Overspecified, 178
- Oxygen
 - excess, 285
 - required, 285
- Partial combustion**, 284
- Partial pressure, 412, 510, 569
- Partial saturation, 538
 - material balance with, 544ff
- Parts per billion (ppb), 62
- Parts per million (ppm), 62
- pascal, 8, 100
- Path variable (function), 610–611
- PEL limits, 495, 533
- Peng-Robinson equation, 461
- Petroleum fraction properties, Appendix K, 1067
- Petroleum physical properties (*see* CD)
- Phase diagrams, 476, 569
- Phase equilibrium, 569
- Phase transitions, 682ff
- Phase, 562, 609
- Physical properties, tables Appendix D, 1036ff (*see also* CD)
- Pitzer acentric factor, 445, table 446, tables Appendix C, 1031ff
- Plasma etching, 730
- Point function, 608
- Pollutants from combustion, 284
- Potential energy (*PE*), 625
- Pound force, 18
- Pound mass, 18
- Pound mole, 43
- Pounds force per square inch (psi), 101
- Power, 615
- ppb (parts per billion), 62
- ppm (parts per million), 62
- Pressure cooker, 503
- Pressure difference, 115
- Pressure, 99ff
 - absolute, 103ff, 107, 402
 - atmospheric, 107
 - barometric, 104, 107
 - comparison of values, 108
 - conversion, 109ff
 - critical, 437ff (*see also* CD)
 - differential pressure measurement, 104ff
 - feet of water, 101
 - gauge, 103
 - head of fluid, 102

- Pressure (*cont.*)
 - measurement, 103
 - measuring devices, 106
 - partial, 412, 510, 567
 - reduced, 438ff
 - relative, 103, 107
 - relief valve, 113
 - units, 8, 9, 100
- Problem solving, 167ff, 184, 186ff
 - guides (*see* CD)
 - sketches for, 169
 - specifications, 177ff
 - strategy for, 168ff, 184ff
- Problem workbook (*see* CD)
- Process
 - analysis, 373
 - equipment (*see* Equipment)
 - feed, 248
 - flowsheet, 306
 - flowsheet modules, 949
 - integration, 343
 - optimization, 373
 - simulators, 938ff
 - steady-state, 345, 609
 - stream symbols, 170
- Property, 396, 609
- Pseudocritical, 440, 446
 - constants for H and He, 440ff
- Pseudo molecular weight, 59–60, 78
- Psychrometric chart (*see* Humidity chart)
- Psychrometric charts for water, 591–592 (*see also* CD)
- p - T plot, 403ff, 478, 515
- Pumping water, 736, 852
- Purge, 355ff
- p - V plot, 403ff, 481, 515
- p - V - T diagram for water, 483
- p - V - T relations
 - ideal gas, 403ff
 - real gas, 436ff
 - water, 483
- Quality**, 481–482
- Rankine (°R)**, 90
- Raoult's Law, 566ff
- Rate, 141, 142, 145, 613–614
- Rate of heat transfer, 613, 619ff
- Real gases, 436ff, 459ff
 - deviations from ideal gases, 436
 - mixtures, 446ff, 667
- Real solution, 865
- Recycle, 346ff
 - stream, 347ff
 - system, 342ff
 - with reaction, 355
 - without reaction, 347ff
- Redlich-Kwong equation, 461
- Reduced variables, 438ff
- Reference conditions, 786
- Reference state, 775, 776
- Reference substance, 493ff
- Reference substance plot, 493, 686
- Reformulated gasoline (*see* alternative fuels)
- Refrigeration cycle, 345
- Reid vapor pressure, 496
- Relative error, 27
- Relative humidity, 539
- Relative pressure, 103, 107
- Relative saturation, 539
- Required air (or oxygen), 284
- Reversible process, 837
- Reynolds number, 23
- Riedel's equation, 685
- Saturated**, 510ff
 - liquid, 479
 - vapor, 479
- SC (*see* standard conditions)
- Selectivity, 240ff
- Semi-batch process, 151
- Sensible heat, 682, 696, 781
- Separator, 306
- Sequential modular, 374, 947
- Sewage sludge, 556
- Shaft work, 615
- SI prefixes, table, 10
- SI units, 7, 8, 404

- Significant figures, 24ff
- Silicon rod manufacturing, 164
- Simplification of an energy balance, 718ff
- Simulation, (*see also* Process simulators)
 - equation based method, 943ff
 - modular method, 947ff
- Simultaneous modular, 374
- Single-pass fraction conversion, 356–357
- Soave-Redlich-Kwong equation, 461
- Soil sorption partition, 595, 602
- Solid, 398
- Solidification, heat of, 682
- Solute, 865
- Solution of cubic equations, 463ff
- Solution of equations, 373, 1069ff,
 - Appendix L
 - linear, 1072, 1078ff
 - nonlinear, 1080ff
 - via Polymath (*see* CD)
- Solution, 49, 59
- Solvent extraction, 596
- Solvent, 865
- Solving problems (*see* Problem solving)
- Species material balances, 261
- Specific gravity, 51ff
- Specific gravity of a gas, 408
- Specific heat (*see* Heat capacity)
- Specific volume, 48
- Specifications, 175
- Splitter, 306, 917
- SRK equation, 461
- Stack gas, 284
- Standard atmosphere, 107
- Standard conditions (SC), 404, table 404
- Standard conditions of temperature, 90
- Standard heat of combustion, 785
- Standard heat of formation, 764ff
 - reference conditions, 786
 - reference data, 767
 - Standard heat of reaction, 769ff (*see also* heat of reaction)
- Standard state, 765
 - for gas, 404
 - for reactions, 765
- State, 396, 608
- State variable (function), 608, 610
- Steady state, 345, 609
- Steady-state system, 138
- Steam tables, 487ff, 699 (*see also* foldout in the back cover and the CD)
 - enthalpies, 699
 - interpolating in, 491
 - specific volume saturated water, 490
- Sterilization, 741
- Stoichiometric coefficient, 226ff, 234
- Stoichiometric ratio, 227, 235
- Stoichiometry, 226ff
- STP (*see* standard conditions)
- Strategy for solving energy balance problems, 723ff
- Strategy for solving material balances, 168ff
- Stream variable, 915
- Subcooled liquid, 479
- Sublimation, 479
- Sublimation pressure, 479
- Submerged combustion, 831
- Subsystem, 306
- Subtraction of units, 12
- Summation of mass or mole fractions, 58, 175, 178
- Supercritical fluid, 438
- Supercritical region, 479
- Superheated vapor, 479
- Surroundings, 609
- Swamp cooler, 904
- Symbols, 172
- Synthesis gas, 80
- System, 137, 609
- System boundary, 137
- Temperature**, 89ff
 - adiabatic combustion (reaction, flame), 807
 - bubble point, 478
 - condensation (*see* dewpoint below)
 - conversion, 92
 - critical, 437ff, CD
 - dewpoint, 510, 573, 889, 891

- Temperature (*cont.*)
 - dry bulb, 886
 - measurement, 94
 - instrument, 94
 - reduced, 438ff
 - scales, 91
 - sensor range, 82
 - units, 8, 9, 90
 - wet bulb, 886
- Temperature interval (ΔT), 90ff
- Temperature-pressure diagram (*see p-T plot*)
- Theoretical air (or oxygen), 284
- Thermal pollution, 554
- Thermodynamic p - H charts, Appendix I, 1065ff
- Thin film deposition, 505
- Tie component, 209
- Time, 8–9, 142, 145
- Toluene p - H chart, 347–348 (*see also CD*), 1065
- Ton (tonne), 8
- Total material balance, 147
- Trace elements, 67
- Transient, 609
- Transient system, 138–139
- Triple point, 477
- T - V plot, 403ff
- Twaddel, 53
- Two phase equilibrium, 919
- Two-phase (region), 479, 481
- Underground storage tanks**, 72
- Underspecified, 178
- Understanding a problem, 168
- UNIFAC, 467
- UNIQUAC, 467
- Unique solution, 175
- Units, 6ff
 - abbreviation, table, 8–10
 - addition of, 12
 - American Engineering (AE), 9
 - conversion of, 14, 17 (*see also inside front cover*)
 - division of, 12
 - fundamental, 7
 - multiplication of, 12
 - of energy, 8–10, 611–612
 - operations with, 12
 - prefixes, 10
 - SI, 9
 - of heat capacity, 690
 - of pressure, 8–10, 100
 - of temperature, 8–9, 90
- Universal scientific units of pressure, 404
- Universe, 837
- Unknowns, 174ff
- Unsteady state, 138, 609
- Unsteady state balances, 970ff
 - energy balance, 984
 - material balance, 972ff
- Unsteady-state dynamic balances, 970ff
- Unsteady-state system, 138ff
- Upper explosive limit (UEL), 534
- U-tube, 104
- Vacuum**, 105
- Validate solutions, 30ff, 183, 185
- van der Waals equation, 461
- Vapor, 478, 485, 510
- Vapor pressure, 478, 485, 510
 - Cox chart, 493
 - extrapolation, 484
 - prediction, 493
 - Reid, 496
- Vapor pressure constants for Antoine equation, Appendix G, 1057
- Vapor trails, 550
- Vapor-inert gas mixture, table 541
- Vaporization, 479–480, 525ff
- Vapor-liquid equilibria, 565ff
- Venturi, 115
- Venturi meter, 863
- Virial equation of state, 461
- Virus, 578
- Vitamin A, 71
- Vitamin C, 71
- VLE (*see Vapor-liquid equilibria*)

- Volume, 9–11
 - reduced, 438ff
- Volumetric flow rate, 56
- Waste analysis**, table, 60
- Water,
 - cycle, 344
 - p - T diagram, 478
 - p - V diagram, 483
 - p - V - T diagrams, 483
 - specific volume saturated, 490
- Watson's equation, 685
- Weight, 18
- Weight fraction, 57
- Well mixed, 307
- Wet basis, 283
- Wet bulb line, 888
- Wet bulb temperature, 886
- Wet oxidation, 484
- Work (W), 614ff, 838ff
 - batch process, 810
 - calculation of, 616
 - electrical, 615
 - engine, 621
 - flow, 615, 659
 - mechanical, 614
 - reversible, 850
 - shaft, 615
 - sign convention, 614
- Yield**
 - based on feed, 241
 - based on theory, 241
 - based on reactant consumed, 241

PROBLEMS WORKBOOK INDEX



Index

A

Absolute pressure14
 Absorption23
 Adiabatic flame temperature149
 Adiabatic process141
 Ammonia synthesis36
 Annealing oven120

B

Blower116
 Bubble point101

C

Combustion31, 40, 42-44, 48, 67
 Compressibility84-86
 Compression ..94-95
 Compressor95
 Concentration7
 Condensation103
 Conversion to units1-4
 Conversion (reactants)39
 Cox chart88
 Crystallizer33-34

D

Density6
 Dew point93, 100, 161, 167
 Displacement meter30
 Distillation25-26
 Dry bulb temperature170
 Dryer110, 159

E

Energy balances134
 Enthalpy calculations126-128
 Equations, solution of21
 Evaporation45-48, 98
 Evaporator136
 Excess reactant39
 Expansion of gas134, 151
 Extensive variable115

F

Flashcombustion48
 Furnace4, 120, 148

G

Gases71
 Gas meter31
 Gauge pressure14
 Gypsum35

H

Heat capacity ...9, 125-126
 Heat exchanger129-130
 Heat of formation143
 Heat of mixing155-157
 Heat of reaction142
 Heat transfer119, 123
 Heat transfer coefficient4
 Humidity93, 158, 161
 Humidity charts.....158-161

I

Ideal gas71-78
 Integral heat of formation.....155
 Intensive variable115
 Isobaric151
 Isotherma151

K

Kay's method87
 Kinetic energy118

L

Limiting reactant39

M

Manometer12-13
 Material balances.....19, 27
 Mechanical energy balance153
 Membranes78-80
 Mixing28
 Mole5
 Mole fraction6, 8

N	
Nozzle2
O	
Orifice meter30
P	
Packed column53
Packing 53
Percent relative humidity 161
Potential energy118
ppb 7
ppm7
Pressure10-14
Pressure gage11
Pressure measurement10
Pressure swing absorption23
Problem solving19
Pseudo critical method 87
Pyrites 48
Pump116
R	
Raoult s Law101
Reactor35, 37, 56, 59, 82, 144
Redlich-Kwong equation84
Relative humidity93, 158, 161
Relative saturation92
Rotameter30

S	
Saturation90-91, 92-93
Separator57
Shock tunnel 139
Solution of equations 21
Standard heat of reaction142
Steam chest135, 137
Specific gravity 6
Specific heat capacity 9
Slurry reactor 56
Spreadsheet21
Still (see distillation)	
Stoichiometry35-39
Sulfur dioxide 48
Sulfuric acid 52-54, 81-86
System47, 117
T	
Temperature conversion 9
Titanium dioxide 55
U	
Units 1
V	
Vapor-liquid separation 57
Vapor pressure88-92, 131-132
W	
Weight fraction 8
Wet bulb temperature 161
Wheatstone bridge 31
Wine 7
Work115, 119, 134, 151-154



CONVERSION FACTORS

Instructions: To convert a given set of units to a desired set, such as in.^3 to m^3 , proceed as follows. Locate the given set of units in the row in the left hand column of a table. Locate the desired set of units in the column heading in the top row of the table. You thus identify a box that has the desired ratio of units. To carry out the conversion, multiply the given set of units by the number in the box. For example, $(14.3 \text{ in.}^3) (1.639 \times 10^{-5} \text{ m}^3 / 1 \text{ in.}^3) = 2.34 \times 10^{-4} \text{ m}^3$.

VOLUME EQUIVALENTS

	in.^3	ft^3	U.S. gal	liters	m^3
in.^3	1	5.787×10^{-4}	4.329×10^{-3}	1.639×10^{-2}	1.639×10^{-5}
ft^3	1.728×10^3	1	7.481	28.32	2.832×10^{-2}
U.S. gal	2.31×10^2	0.1337	1	3.785	3.785×10^{-3}
liters	61.03	3.531×10^{-2}	0.2642	1	1.000×10^{-3}
m^3	6.102×10^4	35.31	264.2	1000	1

MASS EQUIVALENTS

	avoir oz	pounds	grains	grams
avoir oz	1	6.25×10^{-2}	4.375×10^2	28.35
pounds	16	1	7×10^3	4.536×10^2
grains	2.286×10^{-3}	1.429×10^{-4}	1	6.48×10^{-2}
grams	3.527×10^{-2}	2.20×10^{-3}	15.432	1

LINEAR MEASURE EQUIVALENTS

	meter	inch	foot	mile
meter	1	39.37	3.2808	6.214×10^{-4}
inch	2.54×10^{-2}	1	8.333×10^{-2}	1.58×10^{-5}
foot	0.3048	12	1	1.8939×10^{-4}
mile	1.61×10^3	6.336×10^4	5280	1

POWER EQUIVALENTS

	hp	kW	$(\text{ft})(\text{lb}_f)/\text{s}$	Btu/s	J/s
hp	1	0.7457	550	0.7068	7.457×10^2
kW	1.341	1	737.56	0.9478	1.000×10^3
$(\text{ft})(\text{lb}_f)/\text{s}$	1.818×10^{-3}	1.356×10^{-3}	1	1.285×10^{-3}	1.356
Btu/s	1.415	1.055	778.16	1	1.055×10^3
J/s	1.341×10^{-3}	1.000×10^{-3}	0.7376	9.478×10^{-4}	1

HEAT, ENERGY, OR WORK EQUIVALENTS

	(ft)(lb _f)	kWh	(hp)(hr)	Btu	calorie*	joule
(ft)(lb _f)	1	3.766×10^{-7}	5.0505×10^{-7}	1.285×10^{-3}	0.3241	1.356
kWh	2.655×10^6	1	1.341	3.4128×10^3	8.6057×10^5	3.6×10^6
(hp)(hr)	1.98×10^6	0.7455	1	2.545×10^3	6.4162×10^5	2.6845×10^6
Btu	7.7816×10^2	2.930×10^{-4}	3.930×10^{-4}	1	2.52×10^2	1.055×10^3
calorie*	3.086	1.162×10^{-6}	1.558×10^{-6}	3.97×10^{-3}	1	4.184
joule	0.7376	2.773×10^{-7}	3.725×10^{-7}	9.484×10^{-4}	0.2390	1

*The thermochemical calorie = 4.184 J.

PRESSURE EQUIVALENTS

	mm Hg	in. Hg	bar	atm	kPa	psia
mm Hg	1	3.937×10^{-2}	1.333×10^{-3}	1.316×10^{-3}	0.1333	1.934×10^{-2}
in. Hg	25.40	1	3.386×10^{-1}	3.342×10^{-2}	3.386	0.4912
bar	750.06	29.53	1	0.9869	100.0	14.51
atm	760.0	29.92	1.013	1	101.3	14.696
kPa	7.502	0.2954	1.000×10^{-2}	9.872×10^{-3}	1	0.1451
psia	51.71	2.036	6.893×10^{-2}	6.805×10^{-2}	6.893	1

IDEAL GAS CONSTANT R

1.987 cal/(g mol)(K)
 1.987 Btu/(lb mol)(°R)
 10.73 (psia)(ft³)/(lb mol)(°R)
 8.314 (kPa)(m³)/(kg mol)(K) = 8.314 J/(g mol)(K)
 82.06 (cm³)(atm)/(g mol)(K)
 0.08206 (L)(atm)/(g mol)(K)
 21.9 (in Hg)(ft³)/(lb mol)(°R)
 0.7302 (ft³)(atm)/(lb mol)(°R)

MISCELLANEOUS CONVERSION FACTORS

To convert from	To	Multiply by
angstrom	meter	1.000×10^{-10}
barrel (petroleum)	gal	42
centipoise	(newton)(s)/m ²	1.000×10^{-3}
torr (mm Hg, 0°C)	newton/meter ²	1.333×10^2
fluid oz	cm ³	29.57



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