PRENTICE HALL

BASIC PRINCIPLES and CALCULATIONS in PROCESS TECHNOLOGY

T. DAVID GRIFFITH

FREE SAMPLE CHAPTER

SHARE WITH OTHERS

Basic Principles and Calculations in Process Technology

This page intentionally left blank

BASIC PRINCIPLES AND CALCULATIONS IN PROCESS TECHNOLOGY

T. David Griffith

PRENTICE
HALL

New York • Boston • Indianapolis • San Francisco
Toronto • Montreal • London • Munich • Paris • Madrid
Capetown • Sydney • Tokyo • Singapore • Mexico City

Many of the designations used by manufacturers and sellers to distinguish their products are claimed as trademarks. Where those designations appear in this book, and the publisher was aware of a trademark claim, the designations have been printed with initial capital letters or in all capitals.

The author and publisher have taken care in the preparation of this book, but make no expressed or implied warranty of any kind and assume no responsibility for errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of the use of the information or programs contained herein.

For information about buying this title in bulk quantities, or for special sales opportunities (which may include electronic versions; custom cover designs; and content particular to your business, training goals, marketing focus, or branding interests), please contact our corporate sales department at corpsales@pearsoned.com or (800) 382-3419.

For government sales inquiries, please contact governmentsales@pearsoned.com.

For questions about sales outside the U.S., please contact international@pearsoned.com.

Visit us on the Web: informit.com/ph

Library of Congress Cataloging-in-Publication Data

Griffith, T. David.
Basic principles and calculations in process technology / T. David Griffith.
pages cm
Includes bibliographical references and index.
ISBN 978-0-13-338833-6 (hardcover : alk. paper)
1. Chemical engineering. 2. Chemical processes—Mathematical models. I. Title.
TP146.G75 2016
660'.281—dc23
2015020169

Copyright © 2016 Pearson Education, Inc.

All rights reserved. Printed in the United States of America. This publication is protected by copyright, and permission must be obtained from the publisher prior to any prohibited reproduction, storage in a retrieval system, or transmission in any form or by any means, electronic, mechanical, photocopying, recording, or likewise. To obtain permission to use material from this work, please submit a written request to Pearson Education, Inc., Permissions Department, 200 Old Tappan Road, Old Tappan, New Jersey 07675, or you may fax your request to (201) 236-3290.

ISBN-13: 978-0-13-338833-6
ISBN-10: 0-13-338833-6

Text printed in the United States on recycled paper at Edwards Brothers Malloy.
First printing, September 2015

Editor-in-Chief
Mark L. Taub

Signing Editor
Bernard Goodwin

Acquisitions Editor
Laura Lewin

Development Editor
Michael Thurston

Managing Editor
John Fuller

Senior Project Editor
Mary Kesel Wilson

Copy Editor
Deborah Thompson

Indexer
Jack Lewis

Proofreader
Anna V. Popick

Cover Designer
Chuti Prasertsith

Compositor
Shepherd, Inc.

This book is dedicated to the memory of
my chemical engineer father, T. Ed Griffith

This page intentionally left blank

CONTENTS

FOREWORD xv
PREFACE xvii
ACKNOWLEDGMENTS xxi
ABOUT THE AUTHOR xxiii

PART I BASIC PRINCIPLES **1**

CHAPTER 1 INTRODUCTORY CONCEPTS **3**
1.1 Using This Book 4
1.2 Steps for Solving a Problem 5
1.3 Degrees of Freedom 12
1.4 Dimensional Consistency and the Dimensional Equation 16
1.5 The Big Four: Unit Operations of Process Technology 17
1.6 Concluding Comments 19
Problems 20

CHAPTER 2 AREAS, VOLUMES, COMPLEX OBJECTS, AND INTERPOLATION **21**
2.1 Calculating Areas 22
2.2 Calculating Volumes 28
2.3 Complex Objects: Areas and Volumes 33
2.4 Interpolation and Extrapolation 40

2.5 Concluding Comments 46

Problems 46

CHAPTER 3 UNITS OF MEASURE 51

3.1 Time 53

3.2 Length 54

3.3 Volume 55

3.4 Temperature 56

3.5 Mass, Weight, and Force 61

3.6 Vectors 63

3.7 Torque, Moments, and Couples 66

3.8 Density and Specific Gravity 68

3.9 The Mole Unit 69

3.10 Concentrations 72

3.11 Pressure 76

3.12 Work and Power 78

3.13 Accuracy, Precision, and Variance 80

3.14 Engineering Accuracy and Significant Figures 84

3.15 Scientific Notation 85

3.16 The Vernier Scale 86

3.17 Prefixes: M versus m 87

3.18 Concluding Comments 88

References 89

Problems 90

CHAPTER 4 GAS LAWS: PRESSURE, VOLUME, AND TEMPERATURE 93

4.1 Boyle’s Law 94

4.2 Charles’s Law 96

4.3 Absolute Temperature 97
4.4 The Ideal Gas Law 98
4.5 Real Gases 108
4.6 Volumetric Fractions and Mole Fractions 110
4.7 Standard Conditions 111
4.8 Concluding Comments 112
Appendix 4A: Equations of State 113
Problems 119

CHAPTER 5 THERMODYNAMICS: ENERGY, HEAT, AND WORK 123
5.1 Heat and Its Equivalence 127
5.2 The Conservation of Energy and Matter 128
5.3 Work 130
5.4 Heat Capacity 131
5.5 Enthalpy and Internal Energy 135
5.6 Power 138
5.7 Entropy 139
5.8 Reversible versus Irreversible Systems 142
5.9 Functions of State 144
5.10 The Mollier Diagram 145
5.11 Steam Tables 148
5.12 The Entropy of Mixtures 151
5.13 Latent Heat versus Sensible Heat 158
5.14 Free Energy, Chemical Potential, and Entropy 160
5.15 Laws of Thermodynamics 164
5.16 Adiabatic Processes: Compression and Expansion 167
5.17 The Carnot Cycle and Thermodynamic Efficiency 168
5.18 Refrigeration and Heat Pumps 176

5.19 Joule-Thomson Expansion 179
5.20 Turbo-Expanders 181
5.21 Systems 182
5.22 Concluding Comments 186
Appendix 5A: Concepts of Activity and Fugacity 186
Problems 188

CHAPTER 6 PHASE EQUILIBRIA 193
6.1 The Units of Equilibrium: Partial Pressure and Mole Fraction 194
6.2 Equilibrium Vapor Pressure 195
6.3 Chemical Potential 199
6.4 Boiling 200
6.5 Azeotropes 201
6.6 Degrees of Freedom and the Gibbs' Phase Rule 203
6.7 Phase Transitions 206
6.8 Effects of Impurities 208
6.9 Quality, Bubble Point, and Dew Point 210
6.10 Equilibrium Equations 212
6.11 Effects of Mass and Volume 217
6.12 Osmotic Pressure 218
6.13 Ion Exchange 219
6.14 Supercritical Fluids 222
6.15 Concluding Comments 224
Problems 224

CHAPTER 7 CHEMICAL REACTION KINETICS 227
7.1 Effect of Reactant Concentration 228
7.2 Complex Mechanisms with Intermediates 231

7.3 Effect of Temperature 236

7.4 Catalysts 238

7.5 Yield, Fractional Conversion, and Extent of Reaction 241

7.6 Equilibrium Reactions and the Law of Mass Action 248

7.7 Effect of Phase Behavior 250

7.8 Concluding Comments 251

Problems 252

PART II CALCULATIONS: MATERIAL AND ENERGY BALANCES 259

CHAPTER 8 MATERIAL BALANCES 261

8.1 Methodology 262

8.2 The Assumption of Steady-State 273

8.3 Single-Phase Material Balances for Separation Processes 273

8.4 Single-Phase Material Balances for Blending Processes 283

8.5 Multiple-Phase Material Balances 295

8.6 Material Balances with Chemical Reactions 304

8.7 Material Balances in the Real World 313

8.8 Concluding Comments 314

Appendix 8A: Business Economics 315

Problems 320

CHAPTER 9 ENERGY BALANCES 337

9.1 Methodology 338

9.2 Simple Energy Balances 340

9.3 Simultaneous Material and Energy Balances 344

9.4 Simultaneous Balances with Chemical Reactions 351

9.5 Concluding Comments 357

Appendix 9A: Heat of Mixing 358

Problems 362

PART III APPLICATION OF BASIC PRINCIPLES AND CALCULATIONS TO TRANSPORT PHENOMENA **371**

CHAPTER 10 TRANSPORT PHENOMENA: FLUID FLOW **373**

10.1 Shear Rate and Viscosity 375
10.2 Laminar versus Turbulent Flow 382
10.3 Vectors and Tensors 385
10.4 Shell Balances 386
10.5 The Equations of Motion 392
10.6 Dimensional Analysis 393
10.7 The Reynolds Number and the Fanning Friction Factor 396
10.8 The Bernoulli Equation 402
10.9 Non-Newtonian Fluid Flow 412
10.10 Centrifugal Pumps and Feet of Head 413
10.11 Concluding Comments 415
References 416
Problems 416

CHAPTER 11 TRANSPORT PHENOMENA: HEAT TRANSFER **419**

11.1 Heat Conduction 421
11.2 Convection 431
11.3 Combined Conduction and Convection 435
11.4 Radiation 439
11.5 Dimensional Analysis 448
11.6 Shell Balances 456
11.7 Cocurrent versus Countercurrent Heat Transfer 459
11.8 Concluding Comments 462
References 463
Problems 463

CHAPTER 12 TRANSPORT PHENOMENA: MASS TRANSFER 469
12.1 Diffusion 471
12.2 The Entropy of Mass Transport 476
12.3 Shell Balances 477
12.4 Dispersion 481
12.5 Mass Transport in the Real World 482
12.6 Mass-Transfer Processes: Unit Operations 483
12.7 Material and Energy Balances 498
12.8 Cocurrent versus Countercurrent Flow 516
12.9 Dimensional Analysis, the HETP, and Efficiency 518
12.10 Concluding Comments 528
References 529
Problems 530

POSTFACE 535

APPENDIX A ANSWERS TO SELECTED PROBLEMS 537
Chapter 1 537
Chapter 2 537
Chapter 3 538
Chapter 4 538
Chapter 5 538
Chapter 6 539
Chapter 7 539
Chapter 8 539
Chapter 9 546
Chapter 10 547
Chapter 11 547
Chapter 12 548

APPENDIX B CONVERSION FACTORS 551

APPENDIX C GAS CONSTANTS 555

APPENDIX D STEAM TABLES 557

INDEX 593

FOREWORD

Dr. Griffith has assigned himself the challenging, and perhaps impossible, task of writing a book for plant operators with no university background explaining the content of the standard, four-year college chemical engineering curriculum. His aim is to facilitate communication between the operators and engineers in chemical plants, by familiarizing the operators with the science used by engineers and the jargon associated with it.

Dr. Griffith is well positioned to undertake his task, because of years of involvement in plant operations in the petroleum industry. He has shown considerable patience and tenacity at sticking to his goal and providing the industrial community with a book that is perhaps unique for the technical library. Now the operators can get some idea as to the meaning of such terms as material and energy balances, unit operations, equilibrium, entropy, enthalphy, thermal conductivity, diffusivity, and chemical reaction rates, which engineers use in their daily communications.

—R. B. Bird

PREFACE

There is too much detail in science that is too complex for process operators. That was a criticism of the first draft of this book. In addition, not every process technologist will need everything this book provides. However, the book was not written for the lowest common dominator. We cannot know in advance the exact physics to describe a process that an operator may encounter. Instead, this book is meant to educate process technologists by providing the basic principles that govern and explain their operations. It is a language guide for communication between process technologists and chemical engineers.

Why is the discharge from a sales-gas compressor hot when an engineer says the process is "adiabatic," which means that there is no heat transferred? What does a chemical engineer mean when he or she says that a chemical reaction is "second" order and has a "yield" of 60% or an "extent of reaction" of 16.75 mol/mole? What is meant by stating that a high "stress" tensor causes turbulent flow in a long, smooth pipe that has no fittings? Why are the zones in a process furnace called the "radiation" zone and the "convection" zone?

While having a haircut one day in Norma's Barber Shop in Bay City, Texas, I was talking with a former neighbor who happened to be an operator at the nearby South Texas Project Nuclear Power Plant. When he asked what I was doing, I told him about this book. He said that he and his fellow operators used "steam tables" to report values of the steam at the inlet and outlet of the giant turbines that drove the generators making electricity. He confessed that it would really be helpful to know what those numbers meant. This book provides the answer to his request.

Process operations are described by a "foreign" language, the terminology of chemical engineers. Process technologists make things work for those chemical engineers! The objective of this book is to enhance the communication of process operations so as to improve productivity and, most important, safety.

Chemical engineering is one of the broadest areas of technology. Operations range from giant oil refineries down to artificial organs and further down to the realm of nanotechnology on a microscopic scale. Although it encompasses a wide range of applications, the technology is well grounded in fundamental science and engineering principles. It also uses some of the highest forms of mathematics. However, most chemical engineers do not use those higher mathematics after receiving their degrees and going to work. Yet engineers do use the principles that they learned from all of the calculations they performed using that higher mathematics when they were earning their degrees.

This book covers the subject matter taught to chemical engineers, but the presentation of the material in this edition has been rearranged so that the subject of thermodynamics in Chapter 5 is taught before the chapters on material balances and energy balances in Chapters 8 and 9, respectively. Normally, a chemical engineer takes a course on material and energy balances early in his or her education because that subject does not require the higher math used in other areas. But Chapter 5, "Thermodynamics: Energy, Heat, and Work," gives significant insight into processes and it is perhaps the most important chapter in the understanding of the basic physics of process technology.

So, why learn the fundamental science behind the principles and calculations of process technology? The most important answer is safety. We can memorize all sorts of rules and learn different formulas but there will inevitably be an occasion when there is no exact rule for work or no specific method for a calculation. However, with an understanding of the science, we can extrapolate a rule or procedure to fit a situation. In addition, it is a lot easier to learn and remember rules and procedures when we understand the reasoning behind them.

Be forewarned that there is a lot of material to learn in this text. Will a process technologist use all of it? The answer is almost assuredly no, but just about everything in this text will be used by different process technologists at one time or another. In addition, since a technologist does not know what he or she will need in the future, we have attempted to provide as much science as practicable.

As mentioned, the book is organized differently than the coursework that a chemical engineer will encounter. It is arranged so that each chapter builds on its successors. In Chapter 1, "Introductory Concepts," the text begins by explaining how to solve problems. To exercise those skills, Chapter 2, "Areas, Volumes, Complex Objects, and Interpolation," stresses solving problems to calculate areas and volumes. Complex areas and volumes in that chapter teach the reader how to organize the solution of a multiple-step problem. Chapter 3, "Units of Measure," focuses on the units of measure that are used throughout process industries. Then, the science begins. First are the gas laws in Chapter 4, "Gas Laws: Pressure, Volume, and Temperature," which are then used in Chapter 5, "Thermodynamics: Energy, Heat, and Work," to calculate work and changes in the enthalpy of gases. Chapter 6 is "Phase Equilibria," and Chapter 7, "Chemical Reaction Kinetics," examines chemical-reaction-rate expressions.

Next are the most important chapters: Chapter 8, "Material Balances," and Chapter 9, "Energy Balances." Typically, about 80% of the calculations that a chemical engineer will perform during his or her career are from those two chapters. Finally, there are three chapters on transport phenomena; Chapter 10 is "Transport Phenomena: Fluid Flow," which is known as momentum transport. Chapter 11, "Transport Phenomena: Heat Transfer," discusses energy transport, and Chapter 12, "Transport Phenomena: Mass Transfer," covers the details of separation processes that purify materials.

The opening of each chapter includes a list of chapter sections followed by an explanation of why that chapter is important to process technology. Included are example problems showing how to apply the principles and perform the calculations. In addition, figures illustrate what is described in the text. End-of-chapter problems not only include calculations, but also discussion questions to assist the student in putting the principles of process technology into their own words. Finally, appendices are provided for answers to selected problems, conversion factors, ideal gas constants, and steam tables. The tables in the last three appendices are provided so that data can be easily located instead of having to browse through the text.

The subject of transport phenomena mentioned in Chapters 10, 11, and 12 is likely the most mathematically complex subject in undergraduate studies using vectors, tensors, differential equations, and integral calculus. However, I have a bet with R. Byron (Bob) Bird, the lead author of the landmark book *Transport Phenomena,* which is used by almost every chemical engineer in the world, along with the now just published *Introductory Transport Phenomena*, that process technologists can understand its principles without those mathematics, including why fluid flow is called "momentum transport."

To quote the preface from Bird, Stewart, and Lightfoot, *Transport Phenomena* (New York: John Wiley & Sons, 1960), "Obviously there is more material in this book than can be conveniently used in an introductory course. Having some additional material in the book will be helpful to instructors and advanced students and will, in addition, serve as a warning to the [student] that the 'boundaries of the course' do not coincide with the 'boundaries of the subject.'"

In this textbook, some of the advanced material has been put in sidebars within a chapter and appendices at the end of a chapter. The subject matter in those appendices most likely will never be encountered by the vast majority of process technologists. However, it just might be mentioned sometime by someone. In that eventuality, instead of relying on an unpredictable electronic search, the relevant appendix will provide a ready reference with further explanation of what may be an important topic.

—T. David Griffith, Ph.D.
Blessing, Texas

ACKNOWLEDGMENTS

I have had the good fortune to be educated by the "eagles." There have been so many people I have known who are worthy of being acknowledged in this endeavor. To be educated by one of the most outstanding academicians is noteworthy, but to be educated by so many in different fields is almost unbelievable.

Instead of writing about how each has contributed, I have decided to list them in alphabetical order. Most are well known in the fields of chemical engineering and statistics, and need no introduction. They are R. Byron (Bob) Bird, Michael M. (Iron Mike) Donovan, Robert D. Gunn, Joel O. Hougen and his brother Olaf, William G. (Bill) Hunter, Edwin N. Lightfoot, Robert S. Schechter, Warren E. Stewart, and William H. (Bill) Wade.

A special acknowledgement must be given to Professor Emeritus Bird who is also at the top of the list above not only because it was in alphabetical order. His comments on the book have made me think, which resulted in a greatly improved manuscript. This is particularly true when I attempted to use a simple one-word analogy for entropy in the introduction of Chapter 5, "Thermodynamics: Energy, Heat, and Work." I decided that instead of equating entropy as simply a measure of disorder, it would be better to describe the different applications of the concept of entropy to different circumstances and systems. This is called the "reverse pyramid" style of communication which is one of the most effective methods that I learned almost 40 years ago when preparing slides for the presentation of a technical paper.

This page intentionally left blank

ABOUT THE AUTHOR

Dr. T. David Griffith received his B.S. in chemical engineering from The University of Texas at Austin and his Ph.D. from the University of Wisconsin–Madison, then ranked number one in chemical engineering studies. After working in research on enhanced oil recovery (EOR), he and two friends started a small chemical company in Wisconsin specializing in furniture restoration products. Later, his career took a major shift when he developed a record-setting electronic data interchange (EDI) software package for his wife's computer software consulting business, and provided support to users as far away as Australia. Now, he is doing what he enjoys most, teaching in the hydrocarbon processing industry.

In addition to technical papers based on both graduate school and industrial research, he also wrote and published the user manuals for EDI (electronic data interchange) software, with which users set implementation records with trading partners J.C. Penney and Marathon Oil. Griffith says, "One would be amazed by the parallels between teaching students, reporting research results to associates, and supporting business customers over long distance."

In addition to his background in chemical engineering, he was mentored by one of the most outstanding statisticians in the world, William G. Hunter, who had a B.S. and an M.S. in chemical engineering along with an M.S. and a Ph.D. in statistics. Griffith also says that he tries to be practical and takes the approach of understanding processes instead of just working with equations.

This page intentionally left blank

This page intentionally left blank

CHAPTER 4

Gas Laws: Pressure, Volume, and Temperature

4.1 Boyle's Law **94**
4.2 Charles's Law **96**
4.3 Absolute Temperature **97**
4.4 The Ideal Gas Law **98**
4.5 Real Gases **108**
4.6 Volumetric Fractions and Mole Fractions **110**
4.7 Standard Conditions **111**
4.8 Concluding Comments **112**
Appendix 4A: Equations of State **113**
Problems **119**

The majority of process operations involve material that is in a gaseous state. Temperatures can range from –150°F to over 1,400°F with pressures ranging from a vacuum to over 2,000 psi. These conditions are not isolated extremes, but rather conditions that are typically encountered in various hydrocarbon processing units. Given this wide range of operating conditions, it is critical that a process technologist understand the behavior of gases under extreme conditions.

Under "normal" conditions, all gases behave very much like an ideal gas. Those normal conditions range from about a few tens of degrees below 0°F to only several hundred degrees above, and with pressures from a vacuum to only a few atmospheres. However, as just noted, many processes are carried out under conditions that are anything but normal. As we will see, much can be learned about the nature of gases by studying "ideal" gases.

In general, the molecules, or atoms in the cases of the inert gases, are widely spaced. Consequently, their relatively small volume is insignificant and does not interfere with the relationships of pressure, volume, and temperature that we refer to as PVT. But under the extreme conditions of high pressure and low temperature just described, that molecular volume does interfere and causes a gas to behave in a nonideal manner that results in a larger volume. In addition, certain gases, such as Freon coolants, have strong intermolecular forces between the molecules that make them behave in a nonideal manner under less extreme conditions. Those intermolecular forces can be attractive, repulsive, or both, causing the volume to be smaller or larger.

Advanced Material

Appendix 4A at the end of this chapter discusses equations of state, most notably the equations and tables dependent upon the critical pressure and critical temperature of a nonideal gas. It is highly unlikely that a process technologist will ever have to calculate a PVT relationship for a non-ideal gas. However, from time to time he or she may hear terms such as reduced pressure or reduced temperature along with compressibility factor. Reading this appendix is optional.

4.1 Boyle's Law

Simply stated, at a constant temperature the volume and absolute pressure of a gas's given mass are inversely proportional. That is, if the volume of that gas's given mass gas were to be changed by a certain factor, the absolute pressure would be increased by the inverse of that factor. This is known as Boyle's Law and is applicable whether the volume is being increased or decreased. It only holds true for ideal gases.

Putting Boyle's Law into a mathematical expression gives Equation 4.1.

$$V \propto \frac{1}{p} \tag{4.1}$$

In this equation, p is the absolute pressure and V is the volume of a constant amount of gas in terms of either moles or mass. The $\propto$ symbol means that the left side of the equation is proportional to the right side. Think of this symbol as a "proportionality" symbol instead of an "equals" symbol. Figure 4.1 plots the volume of a constant mass amount of gas versus its absolute pressure at a constant temperature and shows the inverse proportional relationship of Equation 4.1.

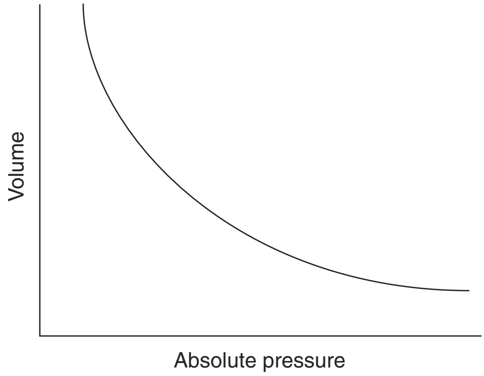

Figure 4.1 Plot of volume V versus pressure p of a gas at a constant temperature

Equation 4.1 implies that at constant temperature, the product of the absolute pressure times the volume is a constant for an ideal gas. This equation can be rewritten to show the effect of a before and after change of pressure and volume at constant temperature, giving us Equation 4.2.

$$p_1V_1 = p_2V_2 \tag{4.2}$$

The subscripts 1 and 2 indicate the states before and after a change. Note that the change may be a change of absolute pressure, a change of volume, or a combination of both.

Stated another way, the product of the absolute pressure times the volume for a given amount of an ideal gas always remains constant for ideal gases.

Equation 4.2 can also be rewritten as shown in Equation 4.3.

$$V_2 = V_1\left(\frac{p_1}{p_2}\right) \tag{4.3}$$

Similarly, it can be arranged as Equation 4.4.

$$p_2 = p_1\left(\frac{V_1}{V_2}\right) \tag{4.4}$$

The subscript of 2 denotes the after condition and the subscript of 1 denotes the before condition.

Also note that a lower case letter p is used for the absolute pressure. We are following the practice of chemical engineers who also use the uppercase fancy script version letter P to denote that the pressure represents the combined effect of static pressure and gravitational forces taking into account the density of the fluid and its relative height. The pressure that is due to a column of fluid above a pressure point is given by Equation 4.5.

$$p = \rho g h \tag{4.5}$$

In this equation, p is the pressure caused by the fluid above the pressure point, ρ is the density of that fluid above the pressure point, g is the gravitational acceleration constant, and h is the total height of the fluid above the pressure point. Note that fluid below the pressure point has no contribution to the pressure; only the height of the fluid above the pressure point affects the pressure.

4.2 Charles's Law

After Boyle's Law was published by Robert Boyle in 1662, it was postulated by Jacques Charles in 1780 and confirmed in 1802 that the volume of a given mass of a gas would vary according to the **absolute temperature** of the gas. At this time, no one knew the true nature of gases.

Charles's Law states that under the condition of constant pressure the volume of a given mass of an ideal gas is directly proportional to its absolute temperature. Put into a mathematical form, Charles's Law becomes Equation 4.6.

$$V \propto T \tag{4.6}$$

In this equation, V is the volume of a fixed amount of gas in terms of either moles or mass and T is the absolute temperature. The linear relationship between volume and temperature is seen in Figure 4.2.

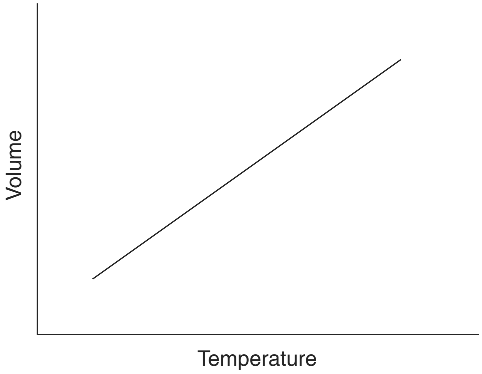

Figure 4.2 Plot of volume V versus absolute temperature T for a gas at a constant pressure

Just as we did before, Equation 4.6 can be rewritten and then used to show volumes before and after a change of temperature, which results in Equation 4.7.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{4.7}$$

The subscripts 1 and 2 indicate the states before and after a change. Remember, absolute temperatures must be used. As mentioned in Chapter 3, "Units of Measure," the absolute temperature scale is measured relative from absolute zero where all motion ceases. In the Celsius temperature scale, where the freezing point of pure water is defined as zero degrees Celsius (0°C) and the boiling point of water at 1 atmosphere of pressure is defined as one hundred degrees Celsius (100°C) absolute zero would be approximately –273.15°C. For the Fahrenheit scale, with 32°F and 212°F being defined as the freezing and boiling points, respectively, absolute zero is –459.67°F. Absolute temperature is discussed in more detail in the next section.

As with Boyle's Law, Equation 4.7 can be rewritten to give Equation 4.8.

$$V_2 = V_1\left(\frac{T_2}{T_1}\right) \tag{4.8}$$

Alternatively, it can be arranged as shown in Equation 4.9.

$$T_2 = T_1\left(\frac{V_2}{V_1}\right) \tag{4.9}$$

4.3 Absolute Temperature

Absolute zero is defined as the temperature at which all motion ceases. When viewing Figure 4.2, we might assume that we could extrapolate the plot line of the gas's volume versus the absolute temperature until the volume is equal to zero. This was initially hypothesized in 1848 and is plotted in Figure 4.3.

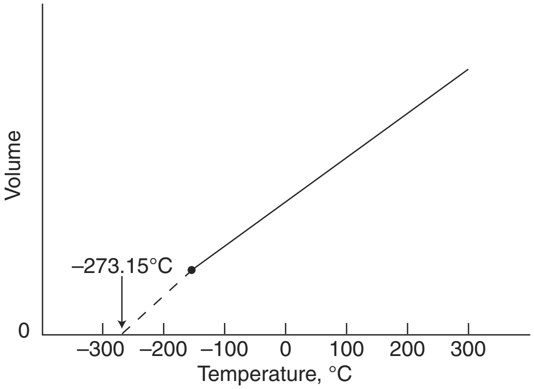

Figure 4.3 Extrapolation to zero volume versus temperature to determine absolute zero

Using the data available at that time, the value of absolute zero was estimated to be –266.66°C compared to the actual value of –273.15°C. In reality, we cannot reach a volume of zero because atoms and molecules do occupy a finite amount of space.

While it may seem logical that the concept of a temperature of absolute zero came from the gas laws, in reality it came from the Second Law of Thermodynamics, which defines an absolute, thermodynamic temperature that is independent of the properties of any particular thermometric body. The law involves the concept of entropy, which is a measure of the disorder of a system. In essence, it prohibits us from getting more work, which is energy, out of a system than has been put into that system. Thus, it prohibits perpetual motion machines. These terms may seem strange—and they are. They are discussed in much more detail in Chapter 5, "Thermodynamics: Energy, Heat, and Work."

4.4 The Ideal Gas Law

We have just seen that the volume of a specified amount of a gas at constant pressure is proportional to the absolute temperature. In addition, we saw that the volume of a specified amount gas at a constant temperature is also inversely proportional to its pressure. We can correctly assume that pressure of a specified amount of gas at a constant volume is proportional to its absolute temperature. Let us also add the fact that the volume at constant pressure and temperature is also proportional to the amount of gas. Similarly, the pressure at constant volume and temperature is proportional to the amount of gas. Thus, these laws and relationships can be combined to give Equation 4.10.

$$pV \propto nT \tag{4.10}$$

Here, n is the number of moles of gas: Again, an *absolute temperature* must be used along with an *absolute pressure*.

Scientists and engineers have defined an ideal gas to be a gas with properties affected only by pressure and temperature. Thus, Equation 4.10 only needs a magical constant so that any one of its variables can be calculated if the other three are known. That constant is the ideal gas constant R and is used to form the Ideal Gas Law given by Equation 4.11.

$$pV = nRT \tag{4.11}$$

Depending on the units of measure for the pressure, the volume, the number of moles, and the absolute temperature, some values for the ideal gas constant R are given in Table 4.1 and Appendix C for different units-of-measure systems.

Table 4.1 Values for R, the Ideal Gas Constant

System	Value with Units of Measure
SI	8.314 (kPa)(m^3)/(kg mol)(°K)
cgs	0.08206 (L)(atm)/(g mol)(°K)
English	0.7302 (ft^3)(atm)/(lb mol)(°R)
English	10.73 (ft^3)(psia)/lb-mol)(°R)

Example 4.1 Volume of an Ideal Gas

Calculate the volume a one-pound mole (1.00 lb_m mol) of an ideal gas occupies at the standard condition of 32°F and 1.00 atmosphere of pressure.

Solution

The information given in the statement of the problem simplifies this problem. We do not need to convert the gas's mass to moles. However, we must convert the temperature in degrees Fahrenheit to the absolute temperature of degrees Rankine. That conversion is

$$T = 32^\circ + 460^\circ = 492^\circ\text{R}$$

Rewriting the Ideal Gas Law given by Equation 4.11 to calculate the volume gives

$$V = \frac{nRT}{p}$$

(*Continues*)

Example 4.1 Volume of an Ideal Gas (*Continued*)

Checking Table 4.1, we see that there is an ideal gas constant R for units of cubic feet, atmospheres, pound moles, and degrees Rankine. Substituting the values for the number of moles, the appropriate ideal gas constant, the absolute temperature, and the pressure gives

$$V = \frac{1.00\ \text{lb mol}\ \big|\ \ 1\ \ \big|\ 0.7302\ (\text{ft}^3)(\text{atm})\ \big|\ 492^\circ\text{R}}{\big|\ 1.00\ \text{atm}\ \big|\ (\text{lb mol})^\circ\text{R}\ \big|}$$

$$= 359\ \text{ft}^3$$

The volume determined in the previous example is important and is usually memorized by engineers. It is the unit volume for 1 lb mol of gas at 32°F and 1 atm or 14.7 psia, which is usually expressed as 359 ft^3/lb mol. Besides the standard volume of 1 lb mol at 32°F and 1 atmosphere, another standard unit volume primarily used by the natural gas industry is defined at 59°F and 1 atmosphere with the value of 379 ft^3/lb mol.

Example 4.2 Volume of 11.0 Pounds of Methane at 80°F and 200 psig

Calculate the volume of 11.0 lbs of methane gas at 200 psig pressure and 80°F.

Solution

There are several steps involved in this calculation. First, we must determine the question, which is to calculate the volume of a quantity of gas at a given temperature and pressure. In a second step, after establishing a basis, we must convert the mass of methane that will be the basis into pound moles. Third, we must convert temperature in degrees Fahrenheit into absolute degrees Rankin and, fourth, convert pressure from psig into psia. Fifth, we must select the appropriate ideal gas constant and use it with a rewritten form of Equation 4.11 to determine the volume of 11.0 lbs of methane gas. Finally, we can substitute the values previously determined into the rewritten equation to calculate the volume.

Basis: 11.0 lb of methane gas

As outlined above, we must calculate the number of pound moles in 11.0 lbs of methane. The molecular weight of methane is about 16.04, which is composed of one atom of carbon with an atomic mass of 12.00 amu and 4 atoms of hydrogen with atomic masses of 1.01 amu:

$$n_{CH_4} = \frac{11.0\ \text{lb}}{16.04\ \text{lb/(lb mol of } CH_4)}$$
$$= 0.686\ \text{lb mol of } CH_4$$

Now, we must convert the temperature to the absolute scale of degrees Rankine:

$$T = 80° + 460° = 540°\text{R}$$

Just as we must use the absolute temperature, we must also use the absolute pressure. We were given the pressure in psig, which is pounds per square in gauge. Gauge pressure is taken relative to the pressure of the atmosphere, which would be 14.7 psia at sea level, and it will have lower pressures at higher elevations. The correction from gauge to absolute pressure at sea level under the standard condition of 1 atmosphere is:

$$p = 200\ \text{psig} + 14.7\ \text{psi} = 214.7\ \text{psia}$$

The rewritten form of Equation 4.11 from Example 4.1 for volume is

$$V = \frac{nRT}{p}$$

Substituting the values for the number of moles, the appropriate ideal gas constant, the absolute temperature, and the absolute pressure gives

$$V = \frac{0.686\ \text{lb mol} \mid 1 \mid 10.73\ (\text{ft}^3)(\text{psia}) \mid 540°\text{R}}{\mid 214.7\ \text{psia} \mid (\text{lb mol})\ °\text{R} \mid}$$
$$= 18.5\ \text{ft}^3$$

Checking for dimensional consistency, we see that lb mol cancels with lb mol, atm cancels with atm, and °R cancels with °R, leaving only ft^3, which is the appropriate unit for our answer of 18.5 cubic feet.

This result is expressed in only 3 digits, although it can be calculated to more. Why?

Hint: What was the number of significant figures in the mass of methane?

There are several ways that Equation 4.11 can be used. The most obvious is to "plug" all of the numbers into the equation each time there is a change and "turn the crank" to calculate a new volume or pressure, or whatever is unknown. However, most of the time not all of the variables are known for this method or it involves a lot of unnecessary arithmetic. In addition, it also involves looking up and confirming one of the gas constants previously described even if they have been memorized.

We could also go back to Boyle's Law and Charles's Law if we were changing only one variable, but due to thermodynamic effects we will discuss in the next chapter, the temperature of a system will usually change whenever the pressure changes.

So, what is the easiest way? Simply use Equation 4.11 to make a ratio of the variables before and after; this gives us Equation 4.12.

$$\frac{p_2 V_2}{p_1 V_1} = \frac{n_2 T_2}{n_1 T_1} \tag{4.12}$$

The subscripts 1 and 2 indicate the before and after states, respectively. Notice that the ideal gas constant R has been canceled because its ratio is unity. We can rewrite Equation 4.12 to calculate a new pressure when a given quantity of gas is compressed and it becomes Equation 4.13.

$$p_2 = p_1 \left(\frac{V_1}{V_2} \right) \times \left(\frac{T_2}{T_1} \right) \tag{4.13}$$

Alternatively, we can rewrite it to calculate the effect on the volume when a gas is compressed to a new pressure and temperature, as shown in Equation 4.14.

$$V_2 = V_1 \left(\frac{p_1}{p_2} \right) \times \left(\frac{T_2}{T_1} \right) \tag{4.14}$$

We could arrange Equations 4.13 and 4.14 to calculate the ratio of the pressures or volumes after and before. That would give us Equation 4.15.

$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right) \times \left(\frac{T_2}{T_1} \right) \tag{4.15}$$

We could also rewrite Equations 4.13 and 4.15 to give us Equation 4.16.

$$\frac{V_2}{V_1} = \left(\frac{p_1}{p_2} \right) \times \left(\frac{T_2}{T_1} \right) \tag{4.16}$$

We can arrange Equation 4.12 as needed to calculate a final pressure, volume, or temperature given the before-and-after states of all of the other variables. Assuming that we understand the Ideal Gas Law and the "PVT" relationship between pressure, volume, and temperature, it is a lot easier to remember just one equation and rearrange it as necessary.

Example 4.3 Effect of Temperature on Pressure of a Batch Reactor

Calculate the expected pressure of a 1.748 ft^3 batch reactor charged at 135 psig and heated from 95°F to 1,650°F.

Solution

Before plugging in a bunch of numbers, look at the problem. Here, we have an overstated problem. This is a sealed batch reactor. It may seem that we need to calculate the amount of gas charged to the reactor, but that is not the case. On the other hand, we may be in a laboratory where the reactor is weighed before and after it is charged. In that case, we could calculate the starting pressure of the gas. However, most times that number is measured and recorded by the experimenter.

Basis: Initial pressure of 135 psig

First, we convert pressure from psig to psia:

$$p_1 = 135 \text{ psig} + 14.7 \text{ psi} = 149.7 \text{ psia}$$

Next, we convert temperatures from degrees Fahrenheit into degrees Rankin:

$$T_1 = 95°\text{F} + 460° = 555°\text{R}$$

and we obtain

$$T_2 = 1650°\text{F} + 460° = 2110°\text{R}$$

Finally, we rewrite Equation 4.12 with $V_2 = V_1$ and $n_2 = n_1$ to give

$$p_2 = p_1\left(\frac{T_2}{T_1}\right)$$

Substituting values for p_1, T_1, and T_2 with their units of measure gives

$$p_2 = 149.7 \text{ psia}\left(\frac{2110°\text{R}}{555°\text{R}}\right) = 569 \text{ psia}$$

In this example, because there were only two units of measure, we did not use the dimensional equation form for the preceding calculation.

In addition to calculating absolute values for pressure, volume, and temperature, as stated above we can calculate ratios that may be more useful. This is demonstrated in Example 4.4.

Example 4.4 Change in Relative Volume

Calculate the relative change in volume when a gas at 165 psig and 95°F is compressed to 855 psig and then heated to 1,250°F.

Solution

Basis: Initial pressure and temperature of 165 psig and 95°F, respectively.

First, we convert pressures from psig to psia:

$$p_1 = 165 \text{ psig} + 14.7 \text{ psi} = 179.7 \text{ psia}$$

and

$$p_2 = 855 \text{ psig} + 14.7 \text{ psi} = 869.7 \text{ psia}$$

Next, we convert temperatures from °F to °R:

$$T_1 = 95°\text{F} + 460° = 555°\text{R}$$

and

$$T_2 = 1250°\text{F} + 460° = 1710°\text{R}$$

Finally, we rewrite Equation 4.12 with $n_2 = n_1$ canceling each other to give

$$\frac{V_2}{V_1} = \left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$$

Substituting values and dimensions yields

$$\frac{V_2}{V_1} = \frac{179.7 \text{ psia} \mid 1710°\text{R}}{869.7 \text{ psia} \mid 555°\text{R}} = 0.637$$

Note that all of the dimensions cancel out only leaving the ratio, which by definition is dimensionless.

Not only are relative changes affected by temperature and pressure, but they are also affected by a *change in the number of moles of gas* when a chemical reaction occurs. Recently, the construction of a number of ethylene crackers has been announced in the Gulf Coast area due to the abundance of natural gas that contains ethane. Those crackers use steam with the ethane in a complex set of chemical reactions that reduce the amount of solid carbon formed, consequently reducing the cracker's "coking" caused by the deposition of elemental carbon. In those crackers, 1 mole of ethane will produce 1 mole of ethylene and 1 mole of hydrogen according to the chemistry of:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

An ethylene cracker is essentially a high-temperature furnace in which ethane flows through the piping, reaching temperatures on the order of 1,500°F in a matter of a few milliseconds. At that temperature, ethane starts to "pyrolyze" and form ethylene with a double bond as two hydrogen atoms are literally broken off. After exiting the furnace, it is quenched almost immediately lest it continue to break down, eventually becoming elemental carbon and molecular hydrogen.

Example 4.5 Effect on Velocity during Ethane Cracking

Approximate the effect on the velocity of ethane as it is cracked in a furnace to form ethylene when it is under 30 psig while flowing at 950 scf/min through a nominal 4-inch schedule-80 pipe entering the furnace at 350°F and exiting at 1,550°F. The ratio of steam to ethane is 1:10.

Solution

Basis:	Ethane at 350°F
Superfluous information:	Initial pressure of 30 psig Flow rate of 950 scf/min Diameter of nominal 4-inch schedule-80 pipe

For all practical purposes, the pressure drop in the pipe will be small as it passes through the furnace and we can set this as

$$p_2 \cong p_1$$

The velocity of the gas is equal to the volumetric flow rate divided by the cross-sectional area of the pipe, which remains constant in the furnace. Thus, the effect on the velocity is essentially equivalent to the increase in the volume of the gas due to the change of temperature and the total number of moles of gas when the ethane is cracked. Therefore, the ratio of the velocities will be:

$$\frac{v_2}{v_1} = \frac{V_2}{V_1}$$

(Continues)

Example 4.5 Effect on Velocity during Ethane Cracking (*Continued*)

Using the Ideal Gas Law, we can write this relationship:

$$\frac{v_2}{v_1} = \frac{V_2}{V_1} = \left(\frac{p_1}{p_2}\right) \times \left(\frac{n_2}{n_1}\right) \times \left(\frac{T_2}{T_1}\right)$$

For our condition with $p_2 \cong p_1$, the ratio of velocities is approximately

$$\frac{v_2}{v_1} = \left(\frac{n_2}{n_1}\right) \times \left(\frac{T_2}{T_1}\right)$$

From the chemistry and the statement of the conditions, we have

$$n_1 = Moles\_ethane + Moles\_steam$$

and

$$Moles\_steam = 0.1 \times Moles\_ethane$$

and then

$$n_1 = 1.1 \times Moles\_enthane$$

Assuming that 100% of the ethane is consumed when cracking to produce the ethylene, we have

$$n_2 = Moles\_ethylene + Moles\_hydrogen + Moles\_steam$$

and

$$Moles\_ethylene = Moles\_hydrogen = Moles\_ethane\_consumed$$

We then have

$$\begin{aligned} n_2 &= 2 \times Moles\_ethylene + Moles\_steam \\ &= 2 \times Moles\_ethane + 0.1 \times Moles\_ethane \\ &= 2.1 \times Moles\_ethane \end{aligned}$$

This gives us

$$\frac{n_2}{n_1} = \frac{2.1 \times Moles\_ethane}{1.1 \times Moles\_ethane}$$

When rewritten, it becomes

$$n_2 = \frac{2.1}{1.1} n_1$$

Adjusting the temperature to *absolute* degrees Rankine gives us:

$$T_2 = 1550°\text{F} + 460° = 2010°\text{R}$$

$$T_1 = 350°\text{F} + 460° = 810°\text{R}$$

From the data, we calculate the following:

$$\begin{aligned}\frac{v_2}{v_1} &= \left(\frac{(2.1/1.1) \times n_1}{n_1}\right) \times \left(\frac{2010°\text{R}}{810°\text{R}}\right)\\ &= 4.74\end{aligned}$$

Thus, we see that there will be an increase of over 4.7 times in the velocity of the gas as it passes through the pipe in the ethylene cracker furnace. This is a dramatic increase in velocity that had to be taken into account when the cracker was designed and operated.

The preceding example was actually a simple problem that has been made more complicated here. The simple solution can provide an estimate for Step 13 of the problem-solving technique in Chapter 1, "Introductory Concepts," in which we judge our results. First, the cracking of ethane into ethylene with the hydrogen being given off doubles the number of moles of gas. Second, the increase of temperature, from 810°R (350°F) to 2,010°R (1,550°F), also more than doubles the volume. Thus, the volume of the gases would be about quadrupled, which approximates and confirms the 4.7 times increase in our previous calculation.

The exact increase in velocity is needed when designing the ethane cracker to insure that there will be sufficient residence time. Also, if the residence time is too great, the ethylene product will continue to crack to carbon and hydrogen gas. However, the actual calculations of the effect on cracking are much more difficult as the increase of the gas volume and thus the velocity is over the length of the pipe, while the temperature increase that more than doubles the volume occurs near the start of the pipe.

4.5 Real Gases

So far, we have worked with ideal gases. However, we live and, more importantly, work in a real world with real gases, and real gases like real people can behave badly. When a gas does behave badly, it is said to be nonideal because it does not obey the Ideal Gas Law. All gases do have nonideal behavior at high pressures and/or low temperatures, so *the two terms are used interchangeably*. However, some gases exhibit nonideal behavior at conditions where other gases exhibit ideal behavior.

Sometimes, as a gas is compressed or cooled before reaching the point at which the volume of the molecules becomes relatively large and thus inhibits a further reduction of volume, there are other attractive or repulsive forces that are generated. Those forces are **van der Waals forces,** which are caused by **dipole moments**. These forces affect the volume of a nonideal gas, as shown in Figure 4.4.

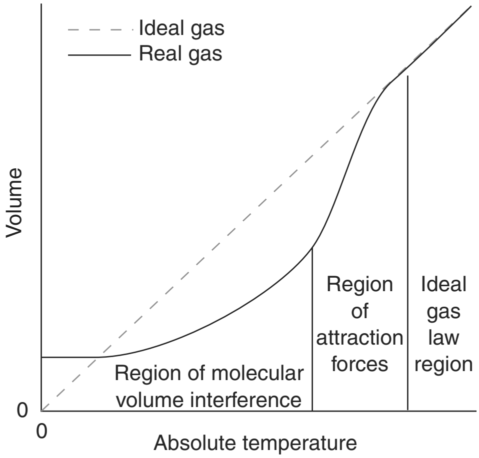

Figure 4.4 Effect of temperature on the volume of a nonideal gas

A dipole moment is an electrostatic force between molecules. Some of the atoms of a gaseous molecule may hold more of the electron cloud due to their higher electronegativity than will the other atoms, resulting in localized charges on the molecule. Oxygen is such an atom because it becomes the location of a greater negative charge. A part of the remaining molecule becomes more positively charged and these molecules are said to be polar. The negatively charged volume of one molecule is attracted to a positively charged volume of another molecule. The force of attraction causes the volume of the gas to be smaller than that predicted by the Ideal Gas Law. The volumes of the electron cloud with the same charge on two different molecules will repel each other.

In addition to permanent dipoles, there can be induced dipoles caused by the temporary location of the electrons as they move about the atoms in a molecule. The induced dipoles are also called *London dispersion forces* or, even more loosely, van der Waals forces. Those forces are controlled by quantum mechanics, which is one of the weirdest branches of physics.

Why Dipoles on Molecules Don't Cancel

We might suppose that since there are an equal number of positive and negative volumes on all of the molecules, there would be an equal number of attractive and repulsive dipole interactions among all of the molecules that would cancel each other. However, this is not the case. Since opposite charges attract, which results in a lowering of energy, probability favors that more of the oppositely charged parts of different relatively close-by molecules will align together as compared to the like-charged parts of other close-by molecules aligning together. This difference in the number of alignments results in a net attractive interaction between all of the molecules since opposite charges attract. The net effect of the greater number of the attractive versus the repulsive dipole moments will be to reduce the volume of a nonideal gas.

Permanent dipole moments do not exist for the diatomic molecules of the elemental gases such as hydrogen, nitrogen, oxygen, fluorine, or chlorine because they share their valence electrons equally. Dipole moments also do not exist for the inert noble gases such as helium, neon, or argon, which are mono-atomic. However, the induced dispersion dipoles can exist.

To account for the discrepancies caused by these previously described forces and other such forces, scientists have developed complicated **equations of state** for nonideal gases; for example, the Ideal Gas Law is an equation of state. Two of those equations of state for nonideal gases with additional terms can be studied in Appendix 4A. Also, because the behavior of nonideal gases varies according to the molecular mass, the differences in the electronegativity of the molecules' atoms, the molecules' volume, and sometimes other contributing factors, those equations of state must use different values for the different parameters of the different gases. Also, different equations of state work better for different gases.

4.6 Volumetric Fractions and Mole Fractions

One major benefit of the behavior of gases is that the volume of one ideal gas in a mixture of ideal gases is equivalent to its mole fraction. For all practical purposes, the volume fractions and the mole fractions of the components of an ideal gas mixture are interchangeable.

We can prove the preceding statement by using the Ideal Gas Law. First, the definition of the mole fraction is given by Equation 4.17.

$$y_i = \frac{n_i}{\sum_{j=1}^{k} n_j} \tag{4.17}$$

For Equation 4.17, if y_i is the mole fraction of component i of a mixture k components of gas, n_i is the number of moles of i, and n_j is the number of moles of component j summed from component 1 to component k. We are using y_i for the mole fraction of a gas so as to be consistent with the nomenclature used later in this text where we will use x_i for the mole fraction of component i in a liquid.

Next, we substitute the Ideal Gas Law to calculate the number of moles n for any component, which gives us Equation 4.18.

$$y_i = \frac{\frac{pV_i}{RT}}{\sum_{j=1}^{k} \frac{pV_j}{RT}} \tag{4.18}$$

Note that all of the terms include $\frac{p}{RT}$, which we can now divide out to obtain Equation 4.19.

$$y_i = \frac{V_i}{\sum_{j=1}^{k} V_j} \tag{4.19}$$

Realizing that the total volume V is the sum of the partial volumes $\sum_{j=1}^{k} V_j$, we can substitute V and rewrite Equation 4.19 as Equation 4.20.

$$y_i = \frac{V_i}{V} \tag{4.20}$$

Equating the volume fraction of gas to its mole fraction is analogous to Dalton's Law of Partial Pressures, which equates the partial pressure of a mixture's gas component to the mole fraction of that mixture times the total pressure. We use the total pressure of the gas in Equation 4.18 and not the partial pressure because we are using the volume fraction based on the total volume and total pressure of our system. If we used the total volume of the system instead of the volume fraction, then we would use the partial pressure of the gas and Equation 4.18 would look something like Equation 4.21.

$$y_i = \frac{\frac{p_i V}{RT}}{\sum_{j=1}^{k} \frac{p_j V}{RT}} \tag{4.21}$$

However, we normally don't think in terms of pressure fractions; instead, we think in terms of volume fractions, which is why we correlate mole fractions with volumetric fractions. In the end, it really makes no difference whether we view the fractions as either volume fractions or pressure fractions.

If the volume and temperature are considered to be constant, then we can rewrite Equation 4.21 to give the **partial pressure** of component *I*, which is found by Equation 4.22.

$$\begin{aligned} p_i &= y_i \sum\nolimits_{j=1}^{n} p_j \Big|_{\text{Constant } V, n, \text{ and } T} \\ &= y_i p_{Total} \end{aligned} \tag{4.22}$$

When considering gas mixtures, the most important is our atmosphere, which consists of approximately 78% nitrogen, 21% oxygen, and 1% other gases. Those percentages are both the volumetric percentages and the mole percentages. To make a gas equivalent to our atmosphere, we would need to take about 4 volumes of nitrogen, 1 volume of oxygen, and add just a touch of "other."

4.7 Standard Conditions

We often see the rating of small compressors or other gas handling equipment given as so many standard cubic feet (SCF) at some pressure (psi) for a specified amount of time. But, what is a standard cubic foot and why is that measurement specified with a pressure?

As we saw with the Ideal Gas Law, the volume of a gas is proportional to the amount of that gas. However, most people do not think in terms of moles of a gas and it is even more difficult to think in terms of the mass of a gas. Yet we can and do think in terms of a volume. The only caveat is that we must set the conditions of the gas's temperature and pressure to equate it to an amount of that gas. Thus, a specific temperature and a specific pressure have been adopted to define the conditions of the gas in a cubic foot and thus the number of moles of that gas in that cubic foot. Usually, when making specification, the acronym S.C. is used to indicate standard conditions or sometimes S.T.P is used for standard temperature and pressure.

Unfortunately, different scientific, engineering, governmental, and even international organizations have adopted different temperatures and pressures. Table 4.2 summarizes those temperatures and pressures per the defining organizations.

Table 4.2 Some Standard Conditions for an Ideal Gas

System	Temperature	Pressure	Volume/Unit
SI	273.15°K	101.325 kPa	22.415 m^3/kg mol
Universal Scientific	0.0°C	760 mm Hg	22.415 L/g mol
American Engineering	491.76°R (32°F)	1 atm	359.05 ft^3/lb mol
Natural Gas Industry	59.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft^3/lb mol

Source: David M. Himmelblau and James B. Riggs, *Basic Principles and Calculations in Chemical Engineering,* eighth ed. (Upper Saddle River, NJ: Prentice Hall, 2012): 353.

Inspection of Table 4.2 shows that the SI, the Universal Scientific, and the American Engineering standard conditions have the same conditions of temperature and pressure. However, they have different mass for their standard volumes, but when volumetric flow rates through compressors and other processing equipment are being reported relative to standard conditions, the volume per unit mole is irrelevant for the purpose of defining the condition of temperature and pressure.

By specifying standard cubic feet for our volume per amount of time, we have specified a mass or rather the number of moles for that amount of time. The pressure term is then added to indicate how much force the compressor will have to work against. As will be seen in the next chapter on thermodynamics, a volume against a pressure is equivalent to a force over a distance that tells us how much work the compressor is capable of performing.

4.8 Concluding Comments

Understanding how gases behave as a function of temperature and pressure is critical to understanding process operations on those gases. This will be seen further in Chapter 5, where work is performed on or performed by gases.

We have seen that the volume of gases is proportional to the number of moles and the absolute temperature of the gas, and inversely proportional to the absolute pressure. The relationship between pressure, volume, moles, and temperature when combined with the ideal gas constant gave rise to the Ideal Gas Law, permitting the calculation of any one of the four independent terms when the other three are known.

In general, most gases at less than a few atmospheres of pressure and with temperatures greater than the extreme cold of cryogenic operations (about −150°F), can be treated as ideal gases. However, when dealing with large volumes of gases as may be the case in the hydrocarbon-processing industries, even small effects caused by a nonideal gas's behavior may have large financial consequences.

Appendix 4A: Equations of State

There are about 20 different equations of state in use. It is beyond the scope of this text to discuss all of them. Most have been incorporated into computer simulations when needed. They have been used in calculations for advanced theoretical work that depend on the calculus of PVT, but they do exist and do provide results with an accuracy of 1% to 2%, which is significantly better than the Ideal Gas Law.

Some of the better-known equations of state are the Benedict-Webb-Rubin, the Clausius, the Holborn, the Kammerlingh-Onnes, the Peng-Robison, the Redlich-Kwong, and the Soave-Redlich-Kwong equations. One of the most commonly used equations is the van der Waals Equation of State.

The van der Waals Equation of State

One of the most frequently used equations of state is the van der Waals equation shown in Equation 4.23.

$$\left(p + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = nRT \tag{4.23}$$

Here, a is a measure of the attraction between the particles and b is the exclusion volume of a mole of particles. As can be seen in Equation 4.23, the form of the van der Waals equation is very similar to that of the Ideal Gas Law seen in Equation 4.11. Values for a and b have been experimentally determined and published for a number of different gases.

In general, the attraction constant a in the first set of terms shows that a lower pressure p will be required for a given volume and temperature.

Similarly, in the second set of terms, the quantity nb permits a larger volume V for a given pressure p and temperature T.

The other equations of state mentioned previously have structures similar to the van der Waals equation, but with additional terms. They all include some type of relationship of a modified pressure term multiplying a modified volume that equates to the number of moles of gas, the gas constant, and the absolute temperature.

While widely used, the van der Waals Equation of State has many limitations. The equation tends to break down when operating near the "critical temperature" and the "critical pressure" of the gas. Unfortunately, those temperatures and pressures are near the temperatures and pressures of some process operations, particularly for natural-gas plants.

Compressibility Factors

Perhaps the best correlation of PVT for real gases uses a compressibility factor modified by an acentric factor that was developed by Kenneth Pitzer ("The Volumetric and Thermodynamic Properties of Fluids. I. Theoretical Basis and Virial Coefficients," *Journal of the American Chemical Society* 77, no. 13, 1955: 3427) based on the **critical temperature** and **critical pressure** of a gas. The **critical point** is defined as the temperature and pressure at which a gas phase of a pure substance becomes indistinguishable from its liquid. There will be further discussion about the critical state in Chapter 6, "Phase Equilibria." All you currently need to know is that the critical temperature and critical pressure of a pure gas is a unique physical property of that gas.

Using the compressibility factor, the ideal gas law equation of state becomes Equation 4.24.

$$pV = znRT \tag{4.24}$$

Here, z is the compressibility factor that corrects the Ideal Gas Law equation of state to a generalized equation of state. The modified compressibility factor z is given by Equation 4.25.

$$z = z^0 + z^1\omega \tag{4.25}$$

Here, ω is the Pitzer acentric factor. Tables have been developed that correlate values for z^0 and z^1 with the reduced temperature and reduced pressure of the gas that are calculated by dividing the absolute temperature and absolute partial pressure of the gas by its critical temperature and critical pressure respectively, as shown in Equations 4.26 and 4.27.

$$T_R = \frac{T}{T_C} \tag{4.26}$$

$$p_R = \frac{p}{p_C} \tag{4.27}$$

Here, T_C and p_C are the critical temperature and pressure for a given gas.

Originally, only the first term, z^0, was correlated with the reduced temperature and pressure. However, it was determined that there still remained a slight error. Later, the Pitzer acentric factor ω was developed that has a constant value unique to the chemical, which multiplies the second compressibility term z^1 in Equation 4.25 and is a function of the reduced temperature and pressure. When z^0 and z^1 are added in Equation 4.25, the overall compressibility factor z for the pure gas can then be used in the generalized equation of state of Equation 4.24.

The value of the compressibility factor's use is that once the critical temperature and critical pressure for any gas is known, we can then use the reduced temperature and reduced pressure to obtain values for z^0 and z^1 without having to perform laboratory PVT experiments. Most gases have already had their critical temperatures and pressures determined. Unfortunately, some PVT experiments may still be required to determine the value of the Pitzer acentric factor ω for gases not already quantified. However, it would not be necessary to carry out an exhaustive number of experiments over a wide range of temperatures and pressures as would be needed for the other equations of state.

Example 4.6 Volume of Ethane

Ethane, C_2H_6, is a component of natural gas and an important reactant for the production of ethylene, which is polymerized to make the polyethylene used for plastic films, grocery bags, and other plastic containers. Ethane is one of the most important chemicals. To determine its relative danger, we can compare its volume at high temperature and pressure to that of an ideal gas. What is the expansion factor for ethane at 100°F and 2,000 psia? Is it more or less dangerous than an ideal gas?

Solution

At this high pressure, ethane will behave as a nonideal gas. Equation 4.24 can be used to give

$$\frac{p_2 V_2}{z_2} = \frac{p_1 V_1}{z_1}$$

(*Continues*)

Example 4.6 Volume of Ethane (*Continued*)

Subscripts 1 and 2 are used to denote before and after conditions. The expansion factor is the ratio of the volume after to the volume before, which can be calculated by rewriting the preceding equation to give

$$\frac{V_2}{V_1} = \frac{z_2 p_1}{z_1 p_2}$$

From Himmelblau and Riggs, *Basic Principles and Calculations in Chemical Engineering (*Prentice Hall, 2012), the critical temperature and critical pressure of ethane are

$$T_C = 305.40°\text{K}$$
$$p_C = 708.1 \text{ psia}$$

From these critical properties, the reduced temperature and pressures are calculated to be

$$T_R = \frac{T}{T_C} = \frac{(100°\text{F} + 460°)\ /\ (1.8\text{R}°/\text{K}°)}{305.40°\text{K}} = \frac{311.11°\text{K}}{305.40°\text{K}} = 1.019$$

and

$$p_R = \frac{p}{p_C} = \frac{2000 \text{ psia}}{708.1 \text{ psia}} = 2.824$$

Abbreviated tables of z^0 and z^1 from Lee and Kessler, *American Institute of Chemical Engineers Journal* 21, (1975), 510–518, as functions of T_C and p_C are shown in Tables 4.3 and 4.4.

Table 4.3 Values of z^0 as a Function of T_R and p_R

			p_R			
T_R |	*0.800*	*1.000*	*1.200*	*1.500*	*2.000*	*3.000*
1.00	0.6353	0.2901	0.2237	0.2583	0.3204	0.4514
1.02	0.6710	0.5146	0.2629	0.2715	0.3297	0/.4547
1.05	0.7130	0.6026	0.4437	0.3131	0.3452	0.4604
1.10	0.7649	0.6880	0.5984	0.4580	0.3953	0.4770
1.15	0.8032	0.7443	0.6803	0.5798	0.4760	0.5042
1.20	0.8330	0.7858	0.7363	0.6605	0.5605	0.5425

Table 4.4 Values of z^1 as a Function of T_R and p_R

T_R	p_R 0.800	1.000	1.200	1.500	2.000	3.000
1.00	–0.0588	–0.0879	–0.0609	–0.0678	–0.0824	–0.1118
1.02	–0.0303	–0.0062	0.0227	–0.0524	–0.0722	–0.1021
1.05	–0.0032	0.0220	0.01059	0.0451	–0.0432	–0.0838
1.10	0.0236	0.0476	0.0897	0.1630	0.0698	–0.0373
1.15	0.0396	0.0625	0.0943	0.1548	0.1667	0.0332
1.20	0.0499	0.0719	0.0991	0.1477	0.1990	0.1095

The acentric factor ω for ethane is

$$\omega_{\text{ethane}} = 0.098$$

Source: Kenneth Pitzer, "The Volumetric and Thermodynamic Properties of Fluids. I. Theoretical Basis and Virial Coefficients," *Journal of the American Chemical Society* 77, no. 13 (1955): 3427.

We were very lucky because Tables 4.3 and 4.4 do not have to be interpolated for temperature. If they did, it would have been more difficult as there would have been two independent variables, T_R and p_R. First one of the tables would have to be interpolated for either the reduced temperature or pressure, obtaining two values which then would have to be interpolated for the other reduced pressure or temperature.

In this example, the reduced temperature is 1.019, which is almost the same as the reduced temperature of 1.02 in Tables 4.2 and 4.3. Inspection of the compressibility values at that reduced temperature shows that z^0 and z^1 do not vary significantly. Thus, we can use values of 0.3297 and 0.4547 for z^0 at p_R of 2.000 and 3.000, respectively, for a T_R of 1.02. Interpolating between those values gives

$$\begin{aligned} z^0 &= 0.3297 + \left(\frac{0.4547 - 0.3297}{3.000 - 2.000}\right) \times (2.824 - 2.000) \\ &= 0.4327 \end{aligned}$$

(Continues)

Example 4.6 Volume of Ethane (*Continued*)

Similarly, the values of z^1 at p_R of 2.000 and 3.000 for T_R of 1.02 are –0.0722 and –0.1021, respectively. Interpolating those values gives

$$\begin{aligned} z^1 &= -0.0722 + \left(\frac{-0.1021 - (-0.0722)}{3.000 - 2.000}\right) \times (2.824 - 2.000) \\ &= -0.0299 \end{aligned}$$

Using Equation 4.25, the compressibility factor for ethane at 100°F and 2,000 psia is calculated by

$$\begin{aligned} z &= z^0 + z^1\omega \\ &= 0.4327 + 0.098 \times (-0.0299) \\ &= 0.4298 \end{aligned}$$

The expansion ratio can now be calculated comparing the volume after to the volume before by

$$\begin{aligned} \frac{V_2}{V_1} &= \frac{z_2 p_1}{z_1 p_2} = \frac{1.0000 \times 2000 \text{ psia}}{0.4298 \times 14.7 \text{ psia}} \\ &= 317 \end{aligned}$$

If the gas had been an ideal gas, the compressibility factor would have been unity and the expansion factor would have been

$$\begin{aligned} \frac{V_2}{V_1} &= \frac{z_2 p_1}{z_1 p_2} = \frac{1.0000 \times 2000 \text{ psia}}{1.0000 \times 14.7 \text{ psia}} \\ &= 136 \end{aligned}$$

Obviously, ethane gas can be more than twice as dangerous as an ideal gas.

The conditions of the preceding example are not that different from what might be encountered in a process operation, so be aware of compressed gases. Ideal gases can be dangerous, but real gases can be even more dangerous.

In addition to Pitzer's work cited above, more information about the use of compressibility factors for mixtures can be found in O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principals, Part II, Thermodynamics*, *Second Edition*. (New York: John Wiley & Sons, 1959): 856–861.

Process gases are generally mixtures. For those gases, we can calculate values for a pseudocritical temperature and a pseudocritical pressure by adding the critical temperature and pressure of each component multiplied by its mole fraction in the gas mixture. In essence, the result is a molar average critical temperature and molar average critical pressure. Though not exact, they are within engineering accuracy.

Nomenclature

ρ	Density, mass per unit volume, Equation 4.5
ω	Pitzer acentric factor, Equation 4.25
n	Number of moles, Equation 4.10
p	Absolute pressure, Equation 4.1
R	Ideal gas constant, Equation 4.11
SC	Standard condition of temperature and pressure, may also be S.C.
STP	Standard temperature and pressure, may also be S.T.P.
T	Absolute temperature, Equation 4.6
v	Velocity, Example 4.5
V	Volume, Equation 4.1
z	Pitzer compressibility factor, Equation 4.24

Problems

1. Write the Ideal Gas Law and briefly define its terms.

2. What is the minimum size of a pressure tank to keep the pressure of 4.0 pounds of methane (molecular weight 16) below 800 psig on a hot day with a temperature of 105°F? (Hint: Be careful of units.)

3. At a constant temperature, if the pressure of an ideal gas increases, does the volume for a given amount of material increase or decrease?

4. At a constant volume and amount, if the temperature of an ideal gas increases, does the pressure increase or decrease?

5. What is the compressibility factor z and why is it used?

6. Gas equations of state such as the Ideal Gas Law use (choose a or b)
  a. absolute temperature scales such as degrees Rankine or degrees Kelvin.
  b. relative temperature scales such as degrees Fahrenheit or degrees Celsius.

7. True or false: For an ideal gas at a constant pressure and temperature, the mole fraction of a component is the same as the volumetric fraction.

8. True or false: "Standard conditions" for gases have been defined by several organizations and are identical in their conditions, although values for temperature and pressure are expressed in different units of measure.

9. According to Boyle's Law, the volume of a fixed amount of gas at a constant temperature is proportional to pressure by which expression (a or b)?
   - **a.** $V \propto \frac{1}{p}$
   - **b.** $V \propto p$
10. Is the pressure in Boyle's Law absolute or gauge?
11. According to Charles's Law, the volume of a fixed amount of gas at a constant pressure is proportional to the temperature by which expression (a or b)?
   - **a.** $V \propto \frac{1}{T}$
   - **b.** $V \propto T$
12. Which of the following temperature scales can be used for Charles's Law: Celsius, Fahrenheit, Kelvin, and/or Rankine?

Given the following data, calculate the volume, V, for exercises 13 through 20:

13. $P = 125$ psia
$T = 600°\text{R}$
$n = 1.2$ lb mol

14. $P = 75$ psia
$T = 700°\text{R}$
$n = 3.2$ lb mol

15. $P = 200$ psia
$T = 800°\text{R}$
$n = 2.3$ lb mol

16. $P = 65$ psia
$T = 650°\text{R}$
$n = 3.8$ lb mol

17. $P = 200$ psig
$T = 400°\text{F}$
$n = 4.1$ lb mol

18. $P = 925$ psig
$T = 760°\text{F}$
$n = 1.7$ lb mol

19. $P = 330$ psig
$T = 1100°\text{F}$
$n = 4.5$ lb mol

20. $P = 500$ psig
$T = 1300$°F
$n = 2.6$ lb mol

For exercises 21 through 24, calculate the pressure, P:

21. $V = 41$ cu.ft.
$T = 800$°R
$n = 3.7$ lb mol

22. $V = 32.0$ cu.ft.
$T = 1100$°R
$n = 4.1$ lb mol

23. $V = 220$ cu.ft.
$T = 300$°R
$n = 2.2$ lb mol

24. $V = 52$ cu.ft.
$T = 1200$°F
$n = 1.7$ lb mol

Given the following, calculate the number of lb mols, n, for exercises 25 through 32:

25. $P = 250$ psia
$V = 17$ cu.ft.
$T = 125$°F

26. $P = 150$ psia
$V = 215$ cu.ft.
$T = 60$°F

27. $P = 75$ psia
$V = 29$ cu.ft.
$T = -40$°F

28. $P = 200$ psia
$V = 120$ cu.ft.
$T = 100$°F

29. $P = 200$ psig
$V = 120$ cu.ft.
$T = 100$°F

30. $P = 100$ psig
$V = 220$ cu.ft.
$T = -150$°F

31. $P = 60$ psig
$V = 20$ cu.ft.
$T = 400°F$

32. $P = 300$ psig
$V = 330$ cu.ft.
$T = 215°F$

33. What would the volume of an ideal gas at 250 psig in a pressure tank of 5 cu.ft. be at 1 atmosphere, assuming no change in temperature?

34. What would the pressure of that ideal gas in problem 33 be if the pressure tank was heated from 80°F to 800°F, assuming no release of the gas?

35. After calculating the new pressure of the gas in the cylinder in problem 34, would the increased temperature be needed to calculate the volume of the gas if it were released to the surroundings at 1 atmosphere, assuming no change in temperature when the gas is released?

36. A 5-gallon tank for propane with a molecular mass of 44.0 weighs 17.0 pounds empty and 36.5 pounds full. What is the volume of the propane if it were a gas at 60°F and 14.7 psia?

37. How many pounds of helium with a mole mass of 4.0 lb/lb mol under 2,265 psig at 78°F are there in a number-44 high-pressure steel cylinder that has a volume of 44 liters?

38. What volume of air in cubic feet would the helium in problem 37 displace if it were released in Denver with an atmospheric pressure of 25 in Hg?

39. A 1-gallon steel can is heated to 280°F to boil out all of its liquid contents. If it were sealed immediately after removing it from the heat, what internal pressure would result as it cools to 90°F, assuming that the initial pressure was 14.7 psia?

40. If the 1-gallon can in problem 39 collapsed when it cooled, what minimum volume would it have?

41. What are the two factors that cause gases to behave in a nonideal fashion?

42. Does the nonideal behavior of a gas vary? If so, describe the effect of temperature and the effect of pressure on that variation.

43. Why is it necessary to use "standard" conditions when specifying the rating of gas-processing equipment?

44. Are standard conditions the same in different industries throughout the world?

45. Which of the four sets of standard conditions are equivalent in terms of temperature and pressure?

46. Why is the volume per unit mole irrelevant when specifying the standard condition of temperature and pressure to measure the flow rate of a gas through process equipment such as a compressor?

INDEX

A

A. See Area, calculating

Absolute pressure
  Boyle's Law, 94–96
  ideal gas law, 98–99, 101
  measuring in psia, 77–78
  plotting enthalpy for steam water, 211
  varying friction forces in piping system causing, 405
  volume of gas inversely proportional to, 113

Absolute temperature
  Carnot heat-engine representation, 172–174
  Charles's Law, 96–97, 204
  compressible fluid flow, 412
  effect of temperature, 237–238
  entropy, 124, 140
  Gibbs free energy, 161
  ideal gas law, 98–103, 106–107
  overview of, 97–98
  Pitzer acentric factor, 114–115
  radiation proportional to, 439–440, 442, 445, 448
  real gases, 108–109
  scales used for calculating, 58–59, 61
  volume of gas proportional to, 113

Absolute zero
  in absolute temperature, 97–98
  in Charles's Law, 97
  defined, 58–59
  not applicable to entropy, 140–141
  Third Law of Thermodynamics and, 166–167

Absorbers (scrubbers)
  cocurrent flow difficult/impossible in, 516
  energy balances not performed on, 502
  HETP when designing, 526–528
  kinetic-energy changes in, 407
  liquid-liquid extractor similar to, 496–497
  mass transport in real world using, 482
  material balances of, 300–304, 328–331
  microstate (information) of fluid in, 155
  operating lines of, 489, 495
  with porous media for distillation, 481–482
  removing impurities in mass transfer, 470
  removing material from gas phase, 484–488
  sorbers as slang term for, 498
  strippers vs., 488–489

Absorption
  adsorption vs., 490
  estimating, 440
  of heat energy, 440
  in mass transfer, 484–488, 498
  phase behavior in, 210

Acceleration
  calculating amount of work without, 79
  in centrifugal pumps, 414
  change of kinetic energy due to, 410–411
  deriving force from mass and, 61–62, 380
  in diffusion and Newtonian physics, 480
  in fluid flow, 406
  force vectors and, 63–64
  in steady-state conditions, 376

Accumulation
  cooling hot oil with heat exchanger, 348
  energy balances methodology, 338–340
  steady-state operations and, 273
  writing material balance equations, 271

Accuracy, as unit of measure, 80–84

Actions, in ion exchange, 220

Activity, concept of, 186–187

Activity coefficient (γ), 126, 186–187

Adiabatic systems
  of Joule-Thomson expansion, 179–180
  mass transfer in, 184
  simultaneous energy balance/chemical reactions, 351–352
  thermodynamic transfer in, 183
  in thermodynamics, 167

Adsorption
  in mass transfer, 490–492
  material/energy balances not applicable to, 499

Adynamic systems
  in energy balances, 340
  in material balances, 265
  overview of, 183–184
American Society for Testing Materials (ASTM) boiling-point curve, 216
Amine scrubber, 301, 484–485
Amine stripper
  efficiency in removing sulfur, 528
  energy balances not applicable to, 502
  material balance of, 300–304
Ammonia gas (NH_3), dissolving into water, 358–361
Amortization of assets, business economics, 318
amu (atomic mass units), 70–71
Anion-exchange resins, 222
Anions
  in deionizer process, 497–498
  ion exchange and, 220
  as negatively charged particles in concentrations, 72–73, 75
Appendices
  answers to selected questions/problems. *See* Problems and selected answers
  business economics, 315–319
  concepts of activity and fugacity, 186–187
  equations of state, 113–119
  gas constants, 555
  heat of mixing, 358–361
  how to use this book, 4
  steam tables. *See* Steam tables
  table of conversion factors, 551–554
Archimedes, 67
Area, calculating
  circle, 24
  complex objects, 33–36, 48–49
  concluding comments, 46
  ellipse, 25
  exterior cylinder, 25–26
  exterior elliptical cylinder, 26–27
  exterior right cone, 27–28
  exterior sphere, 28
  parallelogram, 23
  problems/selected answers, 46–49, 537–538
  rectangle, 22–23
  square, 22
  triangle, 23–24
Arrhenius equation, 237–239, 251–252
Asides, how to use this book, 4
Assets
  in business economics, 315–317
  depreciation or amortization of, 317–318
Assumptions
  with shell balance used for falling film, 392–393
  of steady-state in this text, 273, 277
  troubleshooting process irregularity, 262, 273
ASTM (American Society for Testing Materials) boiling-point curve, 216
Atmospheres of pressure
  ideal gases and, 113
  unit of measure for, 76–77
Atomic mass units (amu), 70–71
Autocatalytic reactions, 238–239
Azeotropes, 201–203, 214
Azeotropic distillation, 202–203
Azeotropic point, 215

B

Balance accounts, business economics, 315
Basic Principles and Calculations in Chemical Engineering (Himmelblau)
  on dimensional equation, 16–17
  on energy balance/enthalpy of reaction, 353
  this book analogous to, 3–4, 261
Basis
  in energy balances methodology, 339
  in material balances methodology, 267
  solving problem by choosing, 6–7
Batch blending
  calculating concentrations using only volumes, 289–290
  calculating volume after, 288–289
  determining how much to add to raise concentrations, 290–293
  in-line blender, 293–295
  using material balances, 284–287
Batch operations
  accumulation in, 263
  batch distilling ethanol-water, 280–283
  liquid-liquid batch extraction, 296–300
Bekenstein, Jacob, 141
Bell-shaped normal curve, data measurements on, 81–82
Bernoulli equation
  change of height, 405–406
  change of kinetic energy, 406–407
  compressible fluid flow, 412
  friction loss factors, 403
  overview of, 402–403
  power requirements for pipeline flow, 408–411
  pressure change of fluid entering vessel, 407–408

- pressure drop of 90 degree elbow, 404–405
- warning about, 402

Binary azeotropes, 202–203
Binary distillation, 494–496
Binary mixtures, plotting K values, 215
Binary-distillation equilibrium curve, McCabe-Thiele diagram, 495, 510
Bit-sol, as non-Newtonian fluid, 413
Black holes
- absorbing heat/Hawking radiation in, 439
- entropy of, 141

Blackbody, 439–440
Black-box unit operations, 498
Blending
- batch blending. *See* Batch blending
- processes. *See* Single-phase material balances, blending processes

Blood, as non-Newtonian fluid, 413
Boiling, 200–201
Boiling point
- ASTM graph curve for mixtures, 216
- heating water in vessel to, 341–342
- osmotic pressure of liquid and elevation, 218
- in phase transitions, 208

Boltzman, Ludwig, 154–155
Boundary layer
- calculating momentum transport in falling film, 389–391
- in dimensional analysis of mass transfer, 520
- fouling factors in heat transfer altering flow at, 439
- in laminar flow, 382–384
- in material balance of mass transfer, 500
- in shell balance of system, 387

Boyle's Law, 94–96, 204–205
Brine rejection, in phase transitions, 207
British Thermal Unit (BTU)
- calculating heat capacity, 132–133
- cooling hot oil with heat exchanger, 348–349
- heating crude oil in furnace, 343–344
- heating water in vessel to boiling, 341–342
- reaction with specified fractional conversion, 355–356
- using Mollier charts, 147–148

Bubble point
- in boiling, 200–201
- in phase transitions, 207–208
- quality diagram for, 210–211

Bullet propane tank, 9–10, 37–39
Business economics
- assets, liabilities, incomes and expenses, 315–317
- depreciation and amortization, 317–318
- discounted return on investment, 318–319
- overview of, 315

C

Calculate
- in energy balances methodology, 339
- in material balances methodology, 268

Calculus
- calculating momentum transport in falling film, 391–392
- differential vs. integral, 374
- as mathematics of change, 377–378

Calibration, accuracy of instrument, 80
Carnot, Sadi, 130
Carnot cycle
- applying divide and conquer to, 9
- reversing for refrigeration/air conditioning, 176–179
- thermodynamic efficiency and, 168–176

Catalysts
- effect on equilibrium, 250
- speeding up chemical reactions, 238–240

Cation-exchange resins, 220–222
Celsius
- calculating heat capacity, 132–133
- conversion to Fahrenheit, 59–61
- nomenclature for, 88
- temperature scales, 56–59

Centrifugal method of separating isotopes, 194
Centrifugal pumps, and feet of head, 413–414
Change, calculus as mathematics of, 377–378
Charles's Law
- calculating degrees of freedom, 204
- overview of, 96–97

Chemical energy, defined, 129–130
Chemical potential (μ)
- in boiling, 201
- calculating, 187
- effects of mass/volume on equilibrium, 217–218
- osmotic pressure affecting, 217–218
- in phases of equilibrium, 199
- thermodynamics of, 162–163

Chemical reaction kinetics
- calculating reaction rates, 242–245
- calculating yield, 240–243
- catalysts, 238–240

Chemical reaction kinetics (*Continued*)
  complex mechanisms with intermediates, 231–235
  concluding comments, 251
  effect of reactant concentration, 228–230
  effect of temperature, 236–238
  effect on phase behavior, 250–251
  equilibrium reactions/Law of Mass Action, 248–250
  extent of reaction in, 245–247
  mechanism, 231–233
  nomenclature, 251–252
  overview of, 227
  phase behavior effect on, 250–251
  problems/selected answers, 252–257, 539–546
  rate limiting step, 235
Chemical reactions
  energy balances simultaneous with, 351–357
  measuring with molecules, 69
  unit operation for, 19
Chemical reactions, material balances with
  conversion, 306–307
  extent of reaction, 305–306
  extent of reaction vs. conversion of limiting reactant, 310–311
  extent of reaction/conversion/yield, 308–310
  limiting reactant, 306
  overview of, 304–305
  with specified fractional conversion, 311–313
  yield, 307–308
Chilton-Colburn j-factor for heat transfer
  dimensional analysis for heat transfer, 449–455
  dimensional analysis for mass transfer, 519, 521
Chromatographic processes, mass transport
  entropy of, 476
  HETP inappropriate for, 526
  industrial preparative chromatographs, 498
  material/energy balances not applicable to, 499
  in real world, 482
  through adsorber, 491
Circle, calculating area of, 24
Closed systems
  mass transfer in, 184
  thermodynamic transfer in, 183
Cocurrent flow
  in heat transfer, 459–461
  in mass transfer, 516–518
Cold heat source, refrigeration, 176
Complex mechanisms with intermediates chemical reaction kinetics, 231–235
Complex objects
  calculating area of, 33–36, 48–49
  calculating volume of, 36–40, 50
  problems/selected answers, 48–50, 537–538
Component vectors, 385
Composition, estimating by material balance, 279–280
Compressibility factor (*z*), 114–119
Compressible fluid flow, 412
Compression
  adiabatic, 167
  calculating with Mollier chart, 147–148
  in positive displacement pumps, 413
  in refrigeration cycle, 176–178
  in reversible vs. irreversible systems, 143
  Compressor, turbo-expander coupled to, 181–182
Concentration
  calculating how much to add in raising, 290–293
  calculating using only volumes, 289–290
  dilution by solvent and, 152–153
  effect of reactant, 228–230
  effect on entropy, 153–154
  effect on entropy and work, 155
  higher to lower enthalpies, 161
  in mass transport by diffusion, 472, 474
  mass/heat transport due to, 470
  as unit of measure, 72–75
Condensation
  equilibrium vapor pressure and, 197–199
  latent heat of, 208
  in phase equilibrium, 209–210
  as phase transition, 206–208
Condenser
  energy balances of distillation column, 502–505, 507–508
  in refrigeration cycle, 176–178
Conduction
  combined convection and, 435–438
  Fourier's Law of Heat Conduction and, 421–423
  heat flux of a process furnace, 425, 427
  heat loss through composite walls, 427–430
  heat-loss rate for glass window, 426–427, 430–431
  molecular activity in, 423
  overview of, 421
  units of measure/conversion factors for, 423
  of various materials, 423–424
Cones
  calculating area of exterior right, 27–28
  calculating volume of, 32
  calculating volume of truncated, 44–45
Confusion, change of entropy, 124
Conservation
  of energy and matter, 128–130, 161
  in First Law of Thermodynamics, 165

  - of mass in chemical reactions, 304
  - when things don't add up, 272–273
  - in writing equations, 270
- Consistency, dimensional, 16–17, 268, 411
- Constant pressure, 133–134, 137–138
- Constant volume, 134–135, 137–138
- Constant-pressure heat-capacity, 133–134, 135–138
- Consumed
  - definition of, 304
  - energy balances methodology, 338–340
  - reaction rate as reactant is, 230
- Continuous-flow method, 296
- Convection
  - combined conduction and, 435–438
  - dimensional analysis for mass transfer by, 518–526
  - heat transfer via, 431–435, 453–456
  - modeling heat transport using shell balance, 456–459
  - single-phase, 431
- Conversion in chemical reactions (degree of completion)
  - basing on limiting reactant, 306
  - for chemical reactions/material balances, 308–310
  - fractional. *See* Fractional conversion
  - of limiting reactant vs. extent of reaction, 310–311
  - overview of, 306–307
- Conversion factors
  - adding for dimensional consistency, 11
  - for heat conduction, 423
  - for horsepower and watts, 79–80
  - for power, 139
  - in problem solving, 11
  - table of, 551–554
  - units of length, 54–55
  - units of temperature, 59–61
  - units of time, 53–54
  - units of volume, 56
- Cooling
  - in adiabatic expansion of hot gas, 167
  - dissolving NH_3 gas into water using, 358–360
  - effect of Joule-Thomson expansion, 179–180, 412
  - hot oil with heat exchanger, 347–349
  - of material, 18
  - natural gas in turbo-expander, 182
  - in phase transitions, 207–208
  - reduction of pressure as gas is, 142
  - in refrigeration, 176–178
  - using heat pumps, 179
  - using ion exchangers for deionized water quality for, 220
- Correlations
  - energy balance, 339
  - material balance, 266–267, 268–271
- Corrosion inhibitors, 238
- Cost of goods sold, business economics, 316–317
- Countercurrent flow
  - in heat transfer, 459–461
  - in mass transfer, 518
- Couples, measuring force, 66–68
- Critical point, in supercritical fluids, 223
- Critical pressure
  - compressibility factors for real gases, 114–119
  - in supercritical fluids, 222–223
  - volume of ethane, 116
- Critical temperature
  - compressibility factors for real gases, 114–119
  - in supercritical fluids, 222–223
  - volume of ethane, 116
- Crude oil(s)
  - chemical potential of, 199, 205
  - heating in furnace, 343–344
  - plotting with ASTM boiling-point curve, 216
- Cryogenic process
  - material or energy balance in, 185
  - for natural gas, 182
- Crystallization
  - altering catalysts with, 238
  - phase behavior in, 210
- Cube, calculating volume of, 28–29
- Cylinder
  - calculating area of, 25–26
  - calculating area of exterior, 26–27
  - calculating volume of, 30
  - calculating volume of elliptical, 31
  - calculating volume of irregular, 37–40

D

- Dalton's Law of Partial Pressures, 110–111, 195
- Darcy-Weisbach friction factor, 401
- Data, in problem solving, 8, 10
- Data sensors, 124
- Datum
  - calculating change of entropy/enthalpy, 144
  - calculating entropy/enthalpy with Mollier chart, 145–148
  - entropy and, 140
- Deceleration, 406
- Degrees Fahrenheit/Celsius, 57
- Degrees of freedom
  - behavior of chemical systems, 203–206
  - calculation of, 13
  - energy balances methodology, 339
  - entropy in systems with no, 141
  - Gibbs' Phase Rule for calculating, 204–205

Degrees of freedom (*Continued*)
  introduction to, 12–15
  material balances methodology, 267
  practical uses of, 8–9, 15–16
Deionized water, 220, 222
Deionizers, 497–498
Del operator (∇), 473
Delta (Δ)
  calculating change of entropy, 141
  calculating work, 130–131
  defined, 79
Density
  Bernoulli equation and, 403, 406, 411
  centrifugal pumps/feet of head and, 414
  as concentration, 72–76
  cooling hot oil with heat exchanger, 348–349
  corrected volumetric flow rate in material balance, 280
  as unit of measure, 68–69
Dependent values, interpolation/extrapolation, 41–44
Dependent variables
  calculating degrees of freedom, 12–16
  defined, 14
  in energy/material balances methodology, 339
Depreciation of assets, business economics, 317–318
Derived units of measure, 52
Detroit Diesel DD15, 175
Dew point, 208–211
Differential calculus, 374, 376, 378
Differential equations
  difficulty of solving, 377–378
  equations of motion requiring, 392, 396
  second-order, 480
  understanding integral calculus through, 374
Diffusion
  comparing transport property definitions, 475
  del (∇) operator and, 473
  dispersion vs., 482
  flow from higher to lower enthalpies, 161
  formulating using shell balances, 477–480
  mass transfer by, 469–475
  Newtonian physics and, 480
  speeding with mechanical agitation, 470
Dilution
  effect on entropy and work, 155
  by solvent, 152–153
Dimensional analysis
  defined, 16
  in heat transfer, 435, 448–456
  in mass transfer, 518–526
  in fluid flow, 393–396
Dimensional consistency
  in Bernoulli equation, 411
  dimensional equation and, 16–17
  judging results in material balances for, 268
Dimensional equation
  calculating lengths of time, 53–54
  dimensional consistency and, 16–17
Dipole moments
  causing clumping in laminar flow, 382
  of free-flowing fluids, 375
  induced, 109
  London dispersion forces, 109
  Van der Waals forces, 109
  overview of, 108–109
Directions, vector measuring, 63–66
Discharge-fluid streams, liquid-liquid extraction, 296
Discounted return on investment (DROI), business economics, 318–319
Dispersion
  in dipoles, 109
  in mass transfer, 481–482
  in porous media, 481–482
  when using HETP for packed columns, 526
Distance, dispersion as function of, 482
Distillation
  azeotropic, 202–203
  batch distilling of ethanol-water, 280–283
  equilibrium vapor pressure in, 195–199
  heat energy driving, 344–345
  in mass transfer, 492–496
  process operations using, 193
Distillation column
  energy balance of, 349–351, 502–509
  kinetic-energy changes in, 407
  material balance of, 275–280, 509–516
  operation of, 492–496
  performance of 100% efficient, 527–528
  as potential upset in process operations, 337–338
  steady-state by jerks processes in, 263
  using HETP when designing, 526–528
  vacuum, 201
  what can go wrong, 508
Divide and conquer
  calculating area of complex objects, 33–36
  calculating thermodynamic efficiency, 175–176
  calculating volume of complex objects, 36–40
  power requirements for pipeline flow, 411
  as problem solving step, 9–10
Doping, 470
Double entry bookkeeping, 316
DROI (discounted return on investment), business economics, 318–319

Dyne, 62–63
Dyne-cm, 68, 78

E

e, logarithms based on, 155–158, 238
E=mc^2, 128, 165
EBP (end bubble point), boiling of mixtures, 200–201
eff (thermodynamic efficiency), 168–176
Efficiency, in mass transfer, 527–528
Einstein, Albert
  conservation of energy and matter, 128
  First Law of Thermodynamics, 165
  and quantum mechanics, 155
Electrical power, entropy and, 149–151
Electromagnetic radiation, 439
Elementary chemical reactions, 231
Ellipse, calculating area of, 25
Elliptical cylinder
  calculating area of exterior, 26–27
  calculating volume of, 31
Emissivity, estimating, 439–442
Emulsions, in multiphase operations, 295
End bubble point (EBP), boiling of mixtures, 200–201
Endothermic processes
calculating free energy, 160–162
  consequences of, 124–125
  equilibrium reactions/Law of Mass Action, 249
  heat energy levels for, 129
  simultaneous energy balance/chemical reactions, 351–352
Energy
  changes of enthalpy/entropy, 124
  conservation of, 128–130
  distribution in equilibrium vapor pressure, 197–198
  effect of temperature on chemical reaction rate, 236–238
  enthalpy and internal, 135–138
  First Law of Thermodynamics and, 165–166
  flowing from higher to lower enthalpies, 160–161
  forms of, 338
  free. *See* Free energy
  heat transfer. *See* Heat transfer
  internal. *See* Internal energy
  kinetic. *See* Kinetic energy
  mechanical. *See* Mechanical energy
  movement of heat. *See* Heat transfer
  potential. *See* Potential energy
  pressure-volume, 338–339
  thermodynamics as science of. *See* Thermodynamics
  used by heat pumps vs. heaters, 179
Energy balances
  concluding comments, 357
  of distillation column, 502–509
  heat of mixing, 358–361
  in mass transfer, 498–502
  methodology, 338–340
  monitoring mass-transfer unit operations, 498–502
  nomenclature, 361
  overview of, 337–338
  problems/selected answers, 362–370, 546–547
  shell balances as, 386–387, 392
  simple, 340–344
  with simultaneous chemical reactions, 351–357
  with simultaneous material balances, 344–351
Energy transfer, in phase equilibrium, 209–210
Engineering accuracy, significant figures and, 84–85
English (Imperial) units
  calculating heat capacity, 132
  measuring density/specific gravity, 68–69
  unit of measure for work, 130
  United States Customary Units developed from, 52
  units of length, 54–55
  units of mass and force, 62–63
  units of torque, 68
  units of volume, 55–56
  units of work and power, 78–80
English Engineering Units, thermal conductivity, 423
Enthalpy
  calculating energy balances, 337
  calculating free energy, 160–162
  calculating using Mollier diagrams, 145–148
  calculating using steam tables, 145–148
  in energy balances of distillation column, 502–509
  of formation, 357
  as function of state, 144–145
  internal energy and, 135–138
  of reaction, 351–357
  in refrigeration cycle, 176–178
  in thermodynamics of all processes, 124
Entropy
  calculating change of, 141
  calculating using Mollier diagrams, 145–148
  calculating using steam tables, 148–151
  in Carnot cycle/thermodynamic efficiency, 173
  depreciation of assets as, 317
  during frictionless adiabatic process, 167

Entropy (*Continued*)
  as function of state, 144–145
  and Gibbs free energy, 163–164
  in Joule-Thomson expansion, 179–180
  latent vs. sensible heat and, 158–160
  of mass transport, 476–477
  as measure of disorder of system, 98, 139
  of mixtures. *See* Mixtures, entropy of
  overview of, 139–142
  in refrigeration cycle, 176–178
  reversible vs. irreversible systems and, 142–144
  Second Law of Thermodynamics and, 166
  in thermodynamics of all processes, 124–125
  Third Law of Thermodynamics and, 166–167
Envelope(s), drawing
  energy balance, 339–340, 350
  material balance in mass transfer, 499–502
  material balance in multi-phase systems, 297, 299–300
  material balance in single-phase systems, 275–278
  material balance methodology for, 265–266
  scientific basis for, 125
Equalities
  counting variables in problem solving, 8–9
  defined, 9
  writing energy balance, 339
  writing material balance, 266–267, 268–271
Equations
  adding conversion factor to, 11
  applying divide and conquer to, 9
  calculating answer in problem solving, 11–12
  calculating degrees of freedom, 12–16
  caution about more variables than, 15
  checking dimensional consistency, 11
  dimensional, 16–17
  inputting data with units, 10
  judging results, 12
  of motion, in fluid flow, 392–393
  solving problem by organizing, 8
  writing energy balance, 339
  writing material balance, 266–271
Equations of state
  compressibility factors, 114–119
  ideal gas law. *See* Ideal gas law
  for nonideal gases, 109
  overview of, 113
  van der Waals, 113–114
Equilibrium. *See also* Phase equilibria
  of absorber in mass transfer, 485–488
  for cocurrent mass transfer, 517–518
  for countercurrent mass transfer, 483–498, 516–518
  of distillation in mass transfer, 494–496
  equations, 212–216
  estimating in natural gas with K values, 213
  in material balance of distillation column, 510, 512–516
  reactions, 248–250
  stages of adsorption in mass transfer, 490–492
  of stripper in mass transfer, 489
  Zeroth Law of Thermodynamics for, 164–165
Error limits, determining, 84–85
Ethane
  calculating volume of, 100–102, 115–118
  condensing in turbo-expander, 181–182
  cracking, 104–106
  separating with de-ethanizer in partial condensers, 515
Ethanol-water
  azeotropic distillation of, 202–203
  blending. *See* Single-phase material balances, blending processes
  material balances in separation processes, 278–283
  specific gravities of mixtures of, 274
Evaporation
  determining exact distribution of fluid flow, 392
  diffusion of liquid during, 477–480
  equilibrium between liquid and vapor and, 209
  estimating for raindrops before hitting ground, 524–526
  heat of vaporization in, 159
  mass transfer by, 183
  process of, 197–199
  rate of energy transfer during, 518
  in refrigeration, 176, 178
Exothermic processes
  calculating free energy, 161–162
  consequences of, 124–125
  heat energy levels for, 129
  in simultaneous energy balance/chemical reactions, 351–352
Expansion
  cooling effect of adiabatic, 167
  isothermal, 169
  Joule-Thomson, 178–180, 412
  in natural gas turbo-expanders, 181–182
  of refrigerant, 177–179
  in reversible vs. irreversible systems, 143
Expenses
  business economics and, 316–317
  from depreciation/amortization of assets, 317–318
Exponential mathematical model, 237–238
Expressions, chemical reaction rate, 233–235

Extent of reaction (ξ)
  calculating, 245–247
  calculating limiting reactant, 306
  conversion of limiting reactant vs., 310–311
  conversion/yield and, 308–310
  material balance/chemical reactions, 305–306
  simultaneous energy balance/chemical reactions, 353–354
Exterior cylinder, area of, 25–27
Exterior right cone, area of, 27–28
Exterior sphere, area of, 28
External reflux ratio, 511
Extract, as discharge-fluid stream, 296
Extraction, liquid-liquid, 496–497
Extrapolation
  determining absolute zero, 97–98
  and interpolation, 40–45

F

Fahrenheit
  calculating heat capacity, 132–133
  conversion to Celsius, 59–61
  nomenclature for, 88
  temperature scales, 56–59
Falling film
  assumptions used in shell balance for, 392–393
  momentum transport in, 387–392
Fanning Friction factor, fluid flow, 396–401
Feet of head, rating centrifugal pumps, 413–414
Fick's first law, rate of diffusion, 472, 474–475, 483
Filtering
  changing concentration's effect on entropy, 154
  reverse osmosis vs., 218
  Second Law of Thermodynamics and, 166
First Law of Thermodynamics, 165–166, 171
First order chemical reactions, 228–230
First-order differential equation, 459
Fixed costs, business economics, 317
Flow rates
  material/energy balances not applicable to internal, 498
  real world material balances and, 313
Fluid flow
  Bernoulli equation, 402–412
  calculus, 377–378
  centrifugal pumps and feet of head, 413–414
  concluding comments, 415
  dimensional analysis, 393–396
  equations of motion, 392–393
  laminar vs. turbulent flow, 382–385
  modeling heat transport using shell balance, 456–459
  nomenclature, 415–416
  non-Newtonian fluid flow, 412–413
  overview of, 373–374
  performing energy balance in distillation column, 350
  problems/selected answers, 416–418, 547
  references, 416
  Reynolds number and Fanning Friction factor, 396–401
  shear rate and viscosity, 375–382
  shell balances, 386–392
  as unit operation for movement of material, 19
  vectors and tensors, 385–386
Foot, as unit of length, 54–55
Foot-pound (ft-lb), 78
Force
  calculating pressure in force per unit area, 76–78
  calculating torques, moments and couples, 66–68
  calculating work, 130–131
  Newton's first law of motion and, 406
  as unit of measure, 61–63
  van der Waals,' 108–109
  vectors, 63–66
Force per unit area, metric system, 379
Forced vs. free convection, 431–432
Forward rate of chemical reaction, 248–250
Fouling factors, affecting heat transfer, 435, 438–439
Fourier's Law of Heat Conduction, 421–423, 475
Fractional conversion
  calculating chemical reaction rates, 243–245
  calculating with limiting reactant, 306–307
  defined, 240
  extent of reaction vs. conversion of limiting reactant, 310–311
  extent of reaction with specified, 354–357
  limiting reactant with specified, 311–313
Fractional yield, 307, 310
Fractionation, 193
Free convection, 431–434
Free energy
  chemical potential and, 162–163
  entropy and, 163–164
  Gibbs free energy, 161–164, 250
  Helmholtz free energy, 161–162
  overview of, 160–162
Freezing
  effect of impurities on phase equilibrium, 209
  melting ice by heating water to produce steam, 340–341
  as phase transition, 206–208
Freezing point, 207–208, 209
Freezing-point depression, 218
French Revolution, and metric system, 52

Friction
  factors for Bernoulli equation, 403
  irreversible systems and, 142–144
  viscous drag vs., 378
Friction factor
  Darcy-Weisbach, 401
  Fanning, 397–401
Frictionless processes
  entropy during adiabatic processes of, 167
  reversible systems and, 142–143
Froude number (Fr), 394
Fugacity, 126, 186–187
Fugacity coefficient (ϕ), 186–187
Functions of state, thermodynamics, 144–145
Fundamental units of measure, 52
Furlong, unit of length in horse racing, 54
Fusion, latent heat of, 208

G

Gas constants, 555
Gas hydrates, 412
Gas laws
  absolute temperature, 97–98
  Boyle's Law, 94–96
  Charles's Law, 96–97
  concluding comments, 112–113
  equations of state, 113–119
  ideal gas law. *See* Ideal gas law
  nomenclature, 119
  overview of, 93–94
  problems/selected answers, 119–122, 538
  real gases, 108–109
  standard conditions, 111–112
  volumetric and mole fractions, 110–111
Gas(es)
  diffusivities of molecules in, 474
  evaporation of liquid through stagnant, 477–480
  phase transitions of, 206–208
  viscosities of various, 381
Gauge pressure
  change in relative volume, 104–105
  defined, 77
  effect of temperature on pressure of batch reactor, 103
  overview of, 77
Gaussian distribution, 81–83
Generally accepted accounting practices (GAAP), 318
Generated
  definition of, 304
  energy balances methodology, 338–340
Gibbs, J. Willard, 199, 204–205
Gibbs free energy
  chemical potential and, 162–163
  effect of catalyst on equilibrium, 250
  and entropy, 163–164
  overview of, 161–162
Gibbs' Phase Rule
  overview of, 204–205
  phase transitions, 206–208
  triple point of phase behavior, 205–206
Glass window
  estimating heat-loss rate through, 426–427
  estimating temperature change in, 434
  free convection heat transport in, 433–434
  heat flux through single-pane vs. double-pane, 436–438
  heat transport and convection in, 430–431
Gram moles
  determining, 70–72
  as unit of measure for concentrations, 73–75
Graphical Methods in the Thermodynamics of Fluid (Gibbs), 154
Graphs
  determining view factor values, 448
  as equations in problem solving, 8
  equilibrium equations using, 214–216
Gravity
  calculating volume after blending using specific, 288–290
  in cocurrent flow, 516–518
  correcting volumetric balance using specific, 272, 279–280
  density and specific, 68–69
  of ethanol-water mixtures, 274
  in liquid-liquid batch extraction, 297–298
  of neutron star overpowering light in black hole, 141
  of specific ethanol-water mixtures, 274
  weight and, 61

H

H. *See* Enthalpy
Half-life, first-order chemical reactions, 230
Hawking, Stephen, 141
Hawking radiation, 142
Heat
  energy balances methodology, 338–340
  energy balances of distillation column, 502–509
  and its equivalence, 127–128
  latent vs. sensible, 158–160
  in refrigeration system, 176–178
  simple energy balances with, 340–344
  simultaneous energy balance/chemical reactions, 351–357

  simultaneous material/energy balances with, 344–351
  thermodynamics implying movement of. *See* Thermodynamics
  unit operation for, 18
  of water to melt ice and produce steam, 340–341
Heat capacity
  adding water to boiler, 345–346
  calculating in thermodynamics, 131–133
  at constant pressure (C_p), 133–134
  at constant volume (C_V), 134–135
Heat exchangers
  cocurrent vs. countercurrent heat transfer in, 459–461
  cooling hot oil with, 347–350
Heat of dissolution, and entropy, 152
Heat of fusion, 159
Heat of mixing, 358–361
Heat of reaction (or heat of formation), 352–357
Heat of solution, 358
Heat of vaporization, 159
Heat pumps, 178–179
Heat transfer
  calculating change of entropy, 141
  cocurrent vs. countercurrent, 459–461
  combined conduction/convection, 435–438
  comparing transport property definitions, 475
  concluding comments, 462
  convection, 431–435
  dimensional analysis of, 448–456
  entropy and, 142–143
  fouling factors, 438–439
  heat conduction, 421–431
  modeling via shell balances, 456–459
  nomenclature, 462–463
  overview of, 419–421
  problems/selected answers, 463–468, 547–548
  radiation, 439–448
  references, 463
  as unit operation for heating of material, 18–19
  what can go wrong in distillation column, 508
Heat transport
  del (∇) operator used in, 473
  in transport phenomena, 374
  as vector, 386
Heat-transfer coefficients
  in convection, 431, 432–435
  in dimensional analysis, 448–456
Height, change of, 405–406
Height equivalent to theoretical plate (HETP), mass transfer, 526–527
Helmholtz free energy, 161–162
Heterogeneous catalysts, 239
Higher-order chemical reactions, 229–230
Himmelblau, Dr. David. *See Basic Principles and Calculations in Chemical Engineering* (Himmelblau)
Homogeneous catalysts, 239–240
Horsepower
  calculating, 139
  as common unit of power, 78
  equivalence of watts and, 79–80
  pipeline flow requirements, 409–411
Hot heat sink, refrigeration, 176
Hydraulic radius
  in Bernoulli equation, 402
  in dimensional analysis for fluid flow, 394–395
Hydrogen sulfide (H_2S) stripper, material balance of, 300–304

I

Ideal gas law
  calculating degrees of freedom, 203–204
  calculating volume of 11.0 pounds of methane, 100–102
  change in relative volume, 104–105
  effect of temperature on pressure of batch reactor, 103
  effect on velocity during ethane cracking, 105–107
  for molar concentration of component, 194–195
  overview of, 98–99
  standard conditions for, 112
  units of constants for, 555
Ideal gases
  Boyle's Law, 94–96
  calculating change in relative volume, 104–105
  calculating volume, 99–100
  Charles's Law, 96–97
  compressible fluid flow, 412
  effect of temperature on pressure of batch reactor, 103
  gases under normal conditions behaving like, 93
  heat/work and, 138
  values for ideal gas constant, 99, 555
Idealized systems, thermodynamic systems for, 183–184
Immiscible fluids
  in concurrent type of mass transfer, 516–518
  extracting fluid from, 296
  interphase transport as two, 432
  in liquid-liquid extraction, 496–497
  in mass transfer processes, 483
  oil and water as, 295

Imperial units. *See* English (Imperial) units
Impurities
  effect on osmotic pressure of liquid, 217–218
  effect on phase transitions, 208–210
Inch, as smallest unit of length, 54–55
Income, business economics, 316
Income accounts, business economics, 315
Income statement, business economics, 315
Incompressible fluid, and Bernoulli equation, 408–411
Independent values, in interpolation/extrapolation, 41–44
Independent variables
  calculating degrees of freedom, 12–16
  defined, 14
  energy balances methodology, 339
  material balances methodology, 267
Individual material balances, 262, 269–271
Induced dipoles, 109
Inefficiency, change of entropy and, 124
Inert gases, atom spacing of, 93–94
Inertia, 61
Information theory, 141
Infrared (IR) light, 234–235
Infrared radiation
  calculating heat from, 448
  calculating solar-heat transfer, 446–448
  estimating value of solar constant, 446
  heating of Earth by, 446
  overview of, 439
Inhibitors, of chemical reactions, 238
Initial bubble point (IBP), boiling of mixtures, 200–201
Initiators, catalysts acting as, 238
In-line mixer
  dispersion through porous media as, 481–482
  example, 293–295
  liquid-liquid batch extraction using, 297–300
  as single-phase batch operation, 296
Insulation
  effects of convection/radiation vs., 439
  heat flux through composite wall, 427–430
  internal reflux increasing with deteriorating, 515
  in process furnace, 420, 444–445
  thermal conductivities of wool/glass, 424
Intangible assets, in business economics, 315–316, 318
Integral calculus
  calculating area of sun and its view factor, 446
  defined, 378
  determining value of *e*, 158
  difficulty of, 374
  solving problems in fluid flow, 386–392
Interfacial tension, 196
intermediate resultant vector, 65–66
Intermediate values, 10
Intermediates
  catalysts acting as, 238
  detecting chemical reactions with, 234–235
Intermolecular forces, 94
Internal energy
  calculating Helmholtz free energy, 161–163
  determining for steam in steam tables, 149, 150
  enthalpy and, 124, 135–138, 338
  enthalpy vs. temperature plot and, 158–159
Internal reflux, material balance of distillation column, 505–507, 510–511, 514–515
Interpolation
  and extrapolation, 40–45
  problems/selected answers, 537–538
  readings of vernier scales, 86–87
Introductory concepts
  concluding comments, 19
  degrees of freedom, 12–16
  dimensional consistency and dimensional equation, 16–17
  nomenclature, 20
  overview of, 3–4
  problem solving. *See* Problem solving, steps for
  problems/selected answers, 20, 537
  unit operations of process technology, 17–19
  using this book, 4–5
Introductory Transport Phenomena (Bird et al.)
  Bernoulli equation applied to pipe flow of incompressible fluid, 409
  del (∇) operator used in, 473
  mass balance in, 472
  modeling mass transfer using theories in, 528
  overview of, 373–374
  signage in heat-transfer process, 445
  turbulent boundary fluid velocity profile reference, 134
Ion exchange
  equilibrium and, 219–222
  Law of Mass Action for, 248
  material balances not applicable to, 499
Ion exchangers
  operating in chromatographic manner, 526
  softening or deionizing water, 497
Ion-exchange resins
  in dispersion, 481
  multiple-phase material balances for, 295–297
  overview of, 497
  with porous media for separation processes, 481–482
  in real world, 483

IR (infrared) light, 234–235
Irreversible process
  change of entropy, 139
  diffusion as, 151
  irreversible vs. reversible systems, 142–144
  Joule-Thomson throttling process as, 179–180
Isenthalpic process, Joule-Thomson expansion, 179–180
Isentropic step, Carnot cycle, 170
Isolated systems, thermodynamic transfer in, 183
Isothermal expansion, Carnot cycle, 169–170

J

Joule, James, 127
Joule-Thomson effect
  in compressible fluid flow, 412
  in heat and its equivalence, 127–128
  in refrigeration system, 178
  in thermodynamics, 179–180
Judge results
  energy balances methodology, 339
  material balances methodology, 268
  steps for problem solving, 12

K

K values, 213–216
Kelvin, Lord, 51
Kelvin scale, 58–59, 88
Kilowatts (kW), calculating power, 139
Kinetic energy
  Bernoulli equation for change of, 406–407
  defined, 128–129
  in energy balances methodology, 339
  in power requirements for pipeline flow, 410–411
Kinetics. *See* Chemical reaction kinetics
Kirchhoff's Law of Thermal Radiation, 442–443
KISS (Keep It Simple, Stupid), 276
kPa (kilopascals), 77

L

Labeling streams, 266
Laboratory thermodynamic systems, 182–185
Laminar flow
  hydraulic radius not applicable for, 395
  as layered flow, 382
  overview of, 382–384
  shear rate/viscosity and, 380
  solving equations of motion for fluid flow, 393
  turbulent flow vs., 384–385
Land, as asset, 318
Latent heat
  vs. sensible heat, 158–160
  of vaporization, 208
Law of Mass Action, 221–222, 248–250
Leading zeroes, 84
Lean oil contact method, 213
Lean oil process, natural gas, 182
Leibniz, Gottfried, 377
Length
  calculating area, 22–25, 28–30
  calculating volume, 29–30
  of major axis, 25–26, 31, 32–33
  of minor axis, 25–26, 31
  as unit of measure, 52, 54–55
Leonard-Jones forces, 375
Levers, calculating torque, 66–68
Liabilities, business economics, 316
Limiting reactant
  calculating, 306
  conversion process, 306–307
  example of, 309
  extent of reaction vs. conversion of, 310–311
  with specified fractional conversion, 311–313
Liquid-liquid equilibrium, 194
Liquid-liquid extraction
  in mass transfer, 496–497
  in multiphase operations. *See* Multiple-phase material balances
  phase behavior in, 210
  problems, 327–328
Liquid(s)
  diffusion through stagnant air of evaporating, 477–480
  diffusivities of molecules in, 474
  ion exchange in, 219–222
  osmotic pressure of, 217–218
  phase transitions of, 206–208
  viscosities of various, 381–382
Liquid-vapor equilibrium, 193–194
Liquid-vapor interface
  in equilibrium vapor pressure, 196–199
  interfacial tension, 196
  plotting K values with graphs, 215
  surface tension, 196, 201
  when boiling in vacuum, 201
Lockheed Super Constellation, 175
Logarithmic behavior, entropy of mixtures, 152
Logarithms
  change of entropy and natural, 155–157
  dilution by solvent and, 152–153
London dispersion forces, 109

M

M vs. m (prefixes), as units of measure, 87–88
Magnitude, vectors measuring, 63–66

Mass
  azeotropes and, 202
  calculating chemical reaction yields, 240–242
  in compressible fluid flow, 412
  conservation of, 304
  converting into molecules using moles, 70
  in cooling hot oil with heat exchanger, 348–349
  effect on equilibrium, 217–218
  as fundamental unit of measure, 52, 61–63
  material balance by, 278–279
  material balance/chemical reactions and, 304
  Newton's first law of motion and, 406
  thermodynamic transfer of, 183–184
Mass transfer
  cocurrent vs. countercurrent flow, 516–518
  concluding comments, 528
  determining exact distribution of fluid flow, 392
  by diffusion, 471–475
  by diffusion with shell balances, 477–480
  dimensional analysis of, 518–526
  dispersion in, 481–482
  effects of mass/volume on equilibrium, 217–218
  efficiency, 527–528
  energy balances of distillation column, 502–509
  entropy of, 476–477
  height equivalent to theoretical plate, 526–527
  material balances of distillation column, 509–516
  nomenclature, 528–529
  overview of, 194, 469–471
  in phase equilibrium, 209–210
  problems and selected answers, 529–534, 548–549
  in real world, 482–483
  as transport phenomena, 374
  transport property definitions, 475
  as vector, 386
Mass Transfer Operations (Treybal), 520
Mass transfer, unit operations
  absorption, 484–488
  adsorption, 490–492
  distillation, 492–496
  liquid-liquid extraction, 496–497
  monitoring with material/energy balances, 498–502
  other processes, 497–498
  overview of, 483
  stripping, 488–489
Mass-transfer coefficients, dimensional analysis, 519–526
Material balances
  blending processes. *See* Single-phase material balances, blending processes
  business economics, 315–319
  with chemical reactions. *See* Chemical reactions, material balances with
  concept of, 261–262
  concluding comments, 314–315
  of distillation column, 509–516
  in mass transfer, 498–502
  monitoring mass-transfer unit operations, 498–502
  multiple-phase. *See* Multiple-phase material balances
  nomenclature, 319
  problems/selected answers, 320–335, 539–546
  in real world, 313–314
  separation processes. *See* Single-phase material balances, separation processes
  shell balances as, 386–387, 392
  with simultaneous energy balances, 344–351
  steady-state process operations, 273
Material balances methodology
  calculate, 268
  classify dependent/independent variables, 267
  define question, 264
  determine degrees of freedom, 267
  determine what is known and unknown for each stream, 266
  drawing envelope(s), 265–266
  identify and label streams, 266
  judge result, 268
  sketching representation, 265
  specify basis, 267
  subscript conventions, 271–272
  understand problem, 264
  when things don't add up, 272–273
  writing equations, equalities, correlations and restrictions, 266–267, 268–271
Matter
  conservation of, 128–130
  First Law of Thermodynamics and, 165–166
McCabe-Thiele diagram, 495, 510, 514–515
Mean, calculating, 82
Mechanical energy
  in Bernoulli equation, 402
  defined, 129–130
  describing fluid flow, 387
  Joule's experiment with, 128, 165
Medical devices, mass transfer by diffusion in, 470
Melting
  ice by heating water to produce steam, 340–341
  as phase transition, 206–208
Melting point, 207–208
Mercaptans, using catalyst, 240
Merox process, using catalyst, 240

Metathetical exchange of ions, 220
Methane
  calculating volume of, 100–101
  cryogenic process producing, 125–126, 182, 184
  Mollier chart for, 145–148
  separating from natural gas with demethanizer, 516
Metric system
  calculating heat capacity, 132
  force per unit area in, 379
  overview of, 52
  process operators in U.S. encountering, 52
  unit of measure for work, 130
  units for mass and force, 62–63
  units of length, 54–55
  units of torque, 68
  units of volume, 56
  units of work and power, 78–80
Microscopic pores, diffusion for fluid flow, 483
Mile, as unit of length, 54–55
Million standard cubic feet per day (MMSCFD), 302
Mixing
  heat of, 358–361
  using mass transfer for, 470
Mixtures
  azeotropic, 202
  of liquids when boiling, 200
  phase transitions of, 206–208
  separation processes of. *See* Single-phase material balances, separation processes
  specific gravities of ethanol-water, 274
Mixtures, entropy of
  determining value of *e*, 157–158
  natural logarithm and change of, 155–157
  overview of, 151–154
  understanding process operation, 154–155
MMSCFD (million standard cubic feet per day), 302
Molal freezing point depression, 209
Molality of substance, osmotic pressure, 217–218
Molar flux
  in absorption, 486
  calculating in water from falling raindrop, 522–524
  in diffusion, 472
  in mass transport equations, 475
Mole fractions
  azeotropes and, 202
  diffusivity and, 472, 474
  effect on adsorption equilibrium, 490–491
  effect on ion exchange equilibrium, 221
  in dimensional analysis of mass transfer, 519–520, 524
  in distillation, 495
  estimating equilibrium with K values, 213–216
  for gas absorber, 485, 487–488
  parts per million and, 75
  in shell balance for mass transfer, 478–480
  for stripper, 489
  as unit of equilibrium, 194–195
  volumetric fractions and, 110–111
Molecular sieves, 497, 499
Molecules
  in convection, 431
  effect of reactant concentration, 228–230
  measuring chemical reactions, 69
  in normal vs. nonideal gases, 93–94
  transport of thermal energy between. *See* Heat transfer
  why dipoles don't cancel on, 109
Moles
  calculating limiting reactant, 306
  change in relative volume and, 104–105
  chemical reaction yields and, 240–242
  chemical reactions/fractional conversion and, 243–245
  extent of reaction, conversion and yield, 308–310
  ideal gas law and, 99
  limiting reaction/specified fractional conversion and, 311–313
  material balances/chemical reactions and, 304
  as unit of measure, 69–72
  velocity during ethane cracking, 106–107
Mollier diagram, 145–148, 176–178
Moments, force, 66–68
Momentum transport
  comparing transport property definitions, 475
  definition of, 378
  del ( ) operator in, 473
  describing fluid flow as, 380
  equating to physical property of viscosity, 375
  in falling film, 387–392
  solving problems in fluid flow, 386–392
  solving problems with shell balances, 385–386
Motion, equations of, 392–393
Movement of material, unit operation for, 18
Multi-batch distillation, 493–494
Multiple-phase material balances
  of H_2S absorber-amine stripper, 300–304
  liquid-liquid batch extraction, 297–300
  overview of, 295–297
  when more than two phases, 304

N

Natural (or Napier) logarithms
  and change of entropy, 155–157
  compressible fluid flow, 412
  determining value of *e*, 157–158
Natural-gas processing, K values, 213–214
Negative degree of freedom, 14
Net profit (loss), business economics, 315
Net transport of radiant heat between objects, 442
Net worth, business economics, 315–316
Newton, Sir Issac, 377
Newtonian fluids, 380, 412
Newton-meters, 68, 79–80
Newton's Laws of Motion
  diffusion, 480
  fluid flow, 387, 406, 408
  mass, 61
  relating force to mass to acceleration, 391
  viscosity, 475
Nomenclature
  areas, volumes, complex objects, interpolation, 46
  chemical reaction kinetics, 251–252
  energy balances, 361
  gas laws, 119
  heat transfer, 462–463
  mass transfer, 528–529
  material balances, 319
  overview of, 20
  phase equilibria, 224
  thermodynamics, 187–188
  transport phenomena (fluid flow), 415–416
  units of measure, 88–89
Nonideal gases
  behavior in extreme conditions, 94
  calculating degrees of freedom, 204
  equations of state for, 109
  equations of state in, 94
  real gases as, 108–109
Nonlinear weighted least squares (NWLS), 81
Non-Newtonian fluid flow, 412–413
Nonzero digits, as significant figures, 84
Normal curves, 81–82
Nusselt number (*Nu*)
  dimensional analysis for heat transfer, 449–453
  dimensional analysis for mass transfer, 519
  estimating heat transfer in process furnace, 454–455
NWLS (nonlinear weighted least squares), 81

O

Omnidirectional pressure, 76
Open systems, thermodynamic transfer in, 183–185
Order of magnitude, scientific notation, 85–86
Organize, solving material/energy balances, 262
Orthogonal, component vectors as, 385
Osmotic pressure, of liquids, 218–219
Overall material balances
  drawing envelope for distillation column, 275–276
  when to perform, 262
  writing equations for, 269–271
Overbars, in significant figures, 84

P

Packed columns
  as absorber type, 484
  using HETP when designing, 526–528
Parallelogram, area of, 23
Parentheses, calculating answer to problems, 11–12
Partial overhead condenser, distillation column, 515–516
Partial pressure, 194–196, 199
Partition coefficients, multiphase operations, 296
Parts per million (ppm), 75
Parts per million (ppmv), 75
Pascal, as SI unit for pressure, 77
PE. *See* Potential energy
Perfume bottle, diffusion from opened, 472
Permanent dipoles, 109
Perpetual motion machines, 165, 166
Phase behavior
  of complex crude-oil–brine emulsion, 199, 205
  effect of chemical reactions on, 250–251
  reverse osmosis governed by, 219
  in separation processes, 194
  of supercritical fluids, 222–223
  triple point of, 205–206
  unit operations relying on phase equilibrium, 210
Phase equilibria
  azeotropes, 201–203
  boiling, 200–201
  chemical potential, 199
  concluding comments, 224
  degrees of freedom, 203–206
  effect of impurities on, 208–210
  effects of impurities, 208–210
  effects of mass and volume, 217–218
  equilibrium equations, 212–216
  equilibrium vapor pressure, 195–199
  ion exchange, 219–222
  of multiphase operations, 296
  nomenclature, 224
  osmotic pressure, 218–219
  overview of, 193–194

  phase transitions, 206–208
  problems/selected answers, 224–226, 539
  quality, bubble point and dew point, 210–211
  supercritical fluids, 222–223
  units of equilibrium, 194–195
Phase transitions, 206–210
Phases
  forced vs. free convection, 431
  in mass transfer by distillation, 470
  processes of two or more. *See* Multiple-phase material balances
  subscript conventions, material balance equations, 271–272
Pitzer, Kenneth, 114
Pitzer acentric factor (ω), 114–115, 117
Planck unit of time, 140–141
Poise, unit of, 380
Polymers, as non-Newtonian fluids, 413
Porous medium, dispersion by flow through, 481–482
Positive displacement pumps, 413
Potential energy
  in Bernoulli equation, 403
  energy balances methodology, 338–339, 348
  kinetic energy changes vs., 407
  in mechanical equivalence of heat/work, 128
  thermodynamics of, 128–129
Pound moles, determining, 70
Pounds, as English unit for mass, 62–63
Pounds per square inch (psi)
  absolute pressure (psia). *See* Absolute pressure
  gauge pressure (psig). *See* Gauge pressure
  overview of, 77
Power
  calculating requirements with Mollier chart, 145
  conversion factors for, 139
  entropy and generation of electrical, 149–151
  requirements for pipeline flow, 408–411
  in thermodynamics, 138–139
  units of work and, 78–80
ppm (parts per million), 75
ppmv (parts per million volume), 75
Prandtl number (*Pr*), 449–455
Precision, as unit of measure, 80–84
Prefixes (M vs. m), as units of measure, 87–88
Preparative chromatography, 498
Pressure
  absolute. *See* Absolute pressure
  Boyle's Law and, 94–96
  calculating for centrifugal pumps, 413–414
  calculating using steam tables, 148–151
  change of fluid entering vessel, 407–408
  Charles's Law and, 96–97
  critical, 114
  drop in pipe, 401
  equilibrium vapor, 195–199
  flowing from higher to lower enthalpies, 161
  fluid height effecting change of, 399–401
  of gases in process operations, 93
  gauge, 77
  heat capacity C_p at constant, 133–134
  osmotic, 217–218
  partial, 194
  units of measure for, 76–78
Pressure, volume and temperature (PVT)
  behavior at high temperatures/pressures, 223
  calculating for nonideal gas, 94
  calculating volume of 11.0 pounds of methane, 100–102
  calculating volume of ideal gas, 99–100
  Carnot cycle and, 169–170
  compressibility factors for real gases, 114–119
  effect of temperature on pressure of batch reactor, 103
  equating volume fraction of gas to its mole fraction, 110–111
  functions of state, 144–145
  internal energy and enthalpy, 135–138
  in normal gases, 94
  in van der Waals equation of state, 113–114
Pressure drop, 404–405, 407
Pressure-volume energy, 338–339
Prism, calculating volume of, 29–30
Probability frequency of measurements, 81–82
Problem solving, steps for
  add appropriate conversion factors, 11
  check dimensional consistency, 11
  count number of variables, 8–9
  define question, 6
  determine a basis, 6–7
  determine available data, 8
  determine data conflicts, 8
  divide and conquer, 9–10
  energy balances methodology, 338–340
  input data with units, 10
  judge results, 12
  material balances. *See* Material balances methodology
  organize equations, 8
  overview of, 5
  read and understand problem, 5–6
  turn cranks, 11–12
  unholy trinity of process, 337–338
Problems and selected answers
  calculating areas, 46–49, 537–538
  calculating volumes, 47–48, 50, 537–538

Problems and selected answers (*Continued*)
  chemical reaction kinetics, 252–257, 539–546
  complex objects, 48–50, 537–538
  energy balances, 362–370, 546–547
  fluid flow, 416–418, 547
  gas laws, 119–122, 538
  heat transfer, 463–468, 547–548
  introductory concepts, 20, 537
  mass transfer, 529–534, 548–549
  material balances, 320–335, 539–546
  phase equilibria, 224–226, 539
  thermodynamics, 188–192, 538–539
  transport phenomena (fluid flow), 416–418, 547
  units of measure, 90–91, 538
Process furnace
  estimating convective heat transfer in, 453–456
  estimating heat-transfer flux in radiant section of, 444–445
  estimating maximum heat flux of, 425, 427
  heat transfer in, 419–420
Process operations
  balancing energy in. *See* Energy balances
  calculations fundamental to. *See* Material balances
  composed of thermodynamic systems, 182–185
  distillation in, 193
  mixtures of entropy and, 154–158
  principles of science governing. *See* Thermodynamics
  as systems, 182
  unholy trinity of process problems, 337–338
Properties, of supercritical fluids, 223
Proportionality symbol, Boyle's Law, 94–96
psi. *See* Pounds per square inch
  as absolute pressure (psia). *See* Absolute pressure
  as gauge pressure (psig). *See* Gauge pressure
  as pounds per square inch, 77
psia. *See* Absolute pressure
psig. *See* Gauge pressure
Purification/separation of material, unit operation for, 19
PVT. *See* Pressure, volume and temperature (PVT)
Pyramid, calculating volume of, 31, 36–37
Pythagorean theorem, 64–66

Q

Q. *See* Heat transfer
q line, 495
Quality, bubble point/dew point, 210–211
Quality control, 262, 337–338
Quantum mechanics, 109, 155
Questions
  in energy balances methodology, 339
  in material balances methodology, 264
  in problem solving, 6

R

r. *See* Radius of circle
R. *See* Ideal gases
Radiation
  calculating solar-heat transfer to roof, 446–448
  and entropy of black holes, 141–142
  estimating heat-transfer flux in radiant section of process furnace, 444–445
  estimating value of solar constant, 446
  Kirchhoff's Law of Thermal Radiation, 442–443
  modeling heat transport using shell balance, 458–459
  overview of, 439–440
  in process operations, 439
  total emissivities of various materials, 441–442
Radioactive atoms, instability of, 230
Radius of circle
  calculating area, 24–25
  calculating exterior area of cylinder, 25
  calculating exterior area of right cone, 27
  calculating exterior area of sphere, 28
  calculating volume of cone, 32
  calculating volume of sphere, 32
Raffinate, as discharge-fluid stream, 296
Rankine scale, 58–59, 88
Rates, chemical reaction
  calculating extent of reaction, 245–247
  calculating fractional conversion, 243–245
  calculating yield, 240–243
  effect of temperature on, 236–238
  equilibrium reactions/Law of Mass Action, 248–250
  overview of, 229–230
  rate-liming step in, 235
  writing expressions of, 233–234
Re. *See* Reynolds number (Re)
Reactant concentration, 228–230, 231–235
Reaction extent. *See* Extent of reaction (ξ)
Reading the problem, problem solving, 5–6
Real gases
  compressibility factors for, 114–119
  as nonideal when behaving badly, 108–109
  overview of, 108–109
  van der Waals equation of state and, 113–114
Real world
  mass transfer in, 482–483
  material balances in, 313–314
  processing thermodynamic systems in, 182–185

Reboiler
  adjusting, 508
  energy balance of distillation column, 507
  material balances on, 515–516
  in modern distillation operations, 494
  in typical distillation column, 492–493
Rectangle
  calculating area of, 22–23
  calculating area of irregular shape, 33–36
  calculating volume of irregular shape, 36–37
  calculating volume of rectangular prism, 29
Rectifying section, distillation column, 493
Reduced pressure, volume of ethane, 116–118
Reduced temperature, volume of ethane, 116–118
Reflections on the Motive Power of Fire and on Machines Fitted to Develop that Power (Carnot), 130
Reflux ratio, 508, 511
Reflux stream
  in distillation, 493
  of distillation column, 493, 494
  energy balances of distillation column, 502, 507
  material balances of distillation column, 509, 511
Refrigeration
  in heat pumps, 178–179
  Joule-Thomson expansion and, 180–181
  thermodynamics and, 176–178
Resins. *See* Ion-exchange resins
Restrictions
  calculating degrees of freedom, 12–16
  writing energy balances with, 339
  writing material balances with, 266–271
Resultant vectors, 385
Reverse osmosis, 218
Reverse rate of chemical reaction, 248–250
Reversible processes
  defined, 139
  entropy measuring change of, 154
  ion exchange as, 221
  reversible vs. irreversible systems, 142–144
Reynolds number (Re)
  calculating, 395–396
  calculating heat-transfer coefficients, 435
  dimensional analysis for fluid flow, 394
  dimensional analysis for heat transfer, 448–455
  dimensional analysis for mass transfer, 519–522
  dimensional analysis using, 16
  vs. Fanning friction factor, 397–401
Rules, input data with units, 10

S

S. *See* Entropy
Scalar measurement, 385
SCF (standard cubic feet), 111–112
Schmidt number (*Sc*), 519–522
Scientific notation, as unit of measure, 85–86
Scrubbers. *See* Adsorbers (scrubbers)
Scum, ion exchange, 220
Second, as smallest unit of time, 53
Second Law of Thermodynamics
  absolute zero in, 58, 98
  countercurrent vs. cocurrent heat transfer and, 461
  endothermic reactions not violating, 250
  entropy of mass transport and, 476
  never having 100% efficient machine, 168
  overview of, 166
Second-order chemical reactions, 228–229
Second-order differential equations, 459, 480
Self-sharpening elution curve, adsorption, 491–492
Sensible heat, 131, 158–160
Sensors, data, 124
Separation processes. *See* Single-phase material balances, separation processes
Separations/purification of material, unit operations for, 19
Shear rate, 375–382, 412–413
Shear stress tensor, 386, 391, 393
Shell balances
  mass transfer and, 477–480
  modeling heat transport, 456–459
  momentum transport in falling film, 387–392
  solving equations of flow, 386–387
Sherwood number, 519–521
Shrodinger, Edwin, 154–155
SI (System International) units
  calculating heat capacity, 132
  defined, 52
  for pressure, 77
  process operators in U.S. encountering, 52
  standard conditions for ideal gas, 112
Sigmoid curve, adsorption, 492
Signage, heat-transfer process, 445
Significant figures, engineering accuracy, 84–85
Simple energy balances, 340–344
Single-phase material balances, blending processes
  adjusting composition by blending two streams, 314
  batch blending, 284–287
  calculating concentrations using only volumes, 289–290
  calculating volume after blending, 288–289
  determining how much to add, 290–293
  in-line mixer example, 293–295
  overview of, 283–284

Single-phase material balances, separation processes
  batch distilling ethanol-water example, 280–283
  density corrected volumetric flow rate, 280
  drawing envelope, 275–276
  estimating composition, 279–280
  material balance by mass, 278–279
  overview of, 273–274
  volumetric material balance on distillation column, 276–278
Single-phase convection, 431
Sintering, altering catalysts with, 238
Sketches
  energy balances methodology, 339
  making and labeling own, 268
  material balances methodology, 265
Slopes, calculus mathematics of, 377–378
Slug, unit for mass, 62
Solar constant, 446–448
Solar heating, 446
Solid-liquid equilibrium, 194
Solids, phase transitions of, 206–208
Solid-vapor equilibrium, 194
Solute, in liquid-liquid extraction, 296
Solvent
  dilution by, 152–153
  in liquid-liquid extraction, 296
Sorbers, 498
Specific gravity
  calculating volume after blending, 288–290
  correcting volumetric balance, 272, 279–280
  density and, 68–69
  of ethanol-water mixtures, 274
  in-line mixer, 294
  liquid-liquid batch extraction, 297–298
  problems/selected answers, 320–327, 539–546
  simultaneous material/energy balances, 346–347, 349
Specified fractional conversion, 311–313
Speed of chemical reactions. *See* Chemical reaction kinetics
Sphere
  calculating area of exterior, 28
  calculating volume of, 32–33, 37–39
Spontaneous processes, 161
Square, calculating area of, 22
Standard conditions, gas laws and, 111–112
Standard cubic feet (SCF), 111–112
Standard deviation (σ), 82–83
Standard heat of reaction, 352–353
State, functions of, 144–145
Static pressure, 76
Steady-state by jerks processes, 263, 273
Steady-state operations
  assumption of, 273
  calculating material balances, 262–263
  changes in internal reflux flow rate of distillation column, 505–507
  energy balances inside distillation columns, 349–350
  evaporation of liquid through stagnant air, 477–480
  heating water in vessel to boiling, 342
  molar or mass-flux vector constant in, 475
  no accumulation in, 263
  rate of heat transport in non-blackbody, 442
  total mass in, 271
Steam
  adding water to boiler to create, 345–346
  simple energy balances using, 340–341
Steam tables
  saturated steam-pressure table, 559–561
  saturated steam-temperature table, 557–559
  superheated steam pressure = 1 psia, 561–562
  superheated steam pressure = 5 psia, 562
  superheated steam pressure = 10 psia, 563
  superheated steam pressure = 14.696 psia, 564
  superheated steam pressure = 20 psia, 565
  superheated steam pressure = 40 psia, 566
  superheated steam pressure = 60 psia, 567
  superheated steam pressure = 80 psia, 568
  superheated steam pressure = 100 psia, 569
  superheated steam pressure = 120 psia, 570
  superheated steam pressure = 140 psia, 571
  superheated steam pressure = 160 psia, 572
  superheated steam pressure = 180 psia, 573
  superheated steam pressure = 200 psia, 574
  superheated steam pressure = 225 psia, 575
  superheated steam pressure = 250 psia, 576
  superheated steam pressure = 275 psia, 577
  superheated steam pressure = 300 psia, 578
  superheated steam pressure = 350 psia, 579
  superheated steam pressure = 400 psia, 580
  superheated steam pressure = 450 psia, 581
  superheated steam pressure = 500 psia, 582
  superheated steam pressure = 700 psia, 584
  superheated steam pressure = 800 psia, 585
  superheated steam pressure = 1000 psia, 586
  superheated steam pressure = 1250 psia, 587
  superheated steam pressure = 1500 and 1750 psia, 588
  superheated steam pressure = 2000 and 2500 psia, 589
  superheated steam pressure = 3000 and 3500 psia, 590

  - superheated steam pressure = 4000 and 5000 psia, 591
  - superheated steam pressure = 6000 psia, 592
  - in thermodynamics, 148–151
- Stefan-Boltzmann law
  - heat-transfer flux in radiant section of process furnace, 445
  - net transport of radiant heat between objects, 442
  - radiation of blackbody, 440
- Stoichiometric coefficient (υ)
  - effect of reactant concentration, 229
  - energy balances with chemical reactions, 354, 370
  - extent of reaction, 246–247, 305–306
  - extent of reaction vs. conversion of limiting reactant, 310–311
  - extent of reaction/conversion/yield, 308–310
  - fractional conversion, 245, 312–313
  - of intermediate product, 233
  - limiting reactant, 306
  - nomenclature, 319
  - yield of chemical reaction, 242–243
- Stoichiometry, 69
- Stokes' Law, 413
- Streams, 339, 470
- Streams, material balance
  - adjusting composition by blending two, 314
  - determining known/unknown for, 266
  - discharge-fluid, 296
  - envelope for distillation column, 275–276
  - envelopes connected by unchanging, 266
  - flowing out of multiphase operations, 295–296
  - identifying/labeling, 266
  - subscript conventions, 271–272
  - writing equations for, 268–271
- Strippers
  - absorbers vs., 488
  - cocurrent flow difficult/impossible in, 516
  - distillation columns vs., 492–493
  - energy balances not performed on, 502
  - kinetic-energy changes in, 407
  - liquid-liquid extractor similar to, 496–497
  - in mass transfer, 488–489
  - operating lines of, 495
  - phase behavior in, 210
  - with porous media for distillation, 481–482
  - removing impurities in mass transfer operations, 470
  - using HETP when designing, 526–528
- Stripping section, distillation column, 493
- Subscript conventions, material balances methodology, 271–272
- Subsystems, process systems, 184–185
- Supercritical fluids, equilibrium and, 222–223
- Superheated steam pressure tables. *See* Steam tables
- Supplemental references, units of measure, 89
- Surface tension
  - boiling in vacuum and, 201
  - at liquid-vapor interface, 196
- SWAG (scientific wild-ass guess), thermodynamics, 128
- System International units. *See* SI (System International) units
- Systematize, solving material/energy balances, 262
- Systems
  - process operations as, 182–185
  - thermodynamics and, 182–185

T

- *T*. *See* Absolute temperature
- Tables
  - adding conversion factors from data to, 11
  - as equations in problem solving, 8
  - equilibrium equations using, 212–213
  - interpolation and extrapolation of, 40–44
  - steam. *See* Steam tables
- Tangible assets, business economics, 315, 317
- Temperature
  - absolute. *See* Absolute temperature
  - Boyle's Law and, 94–96
  - calculating using steam tables, 148–151
  - critical, 114
  - effecting chemical reaction kinetics, 236–238
  - of gases in process operations, 93
  - heat transfer and. *See* Heat transfer
  - mass transport and heat transport due to, 470
  - as measure of energy in system, 56
  - nomenclature for, 88
  - PVT. *See* Pressure, volume and temperature (PVT)
  - simple energy balances with, 340–344
  - simultaneous energy balance/chemical reactions, 351–357
  - simultaneous material/energy balances, 344–351
  - vs. time in phase transitions, 207
  - units of measure, 56–61
- Tensors, in fluid flow, 374, 386
- Terminology, chemical engineering, 4
- Ternary azeotropes, 202
- Tetrahedral pyramid, 36–37
- Theoretical yield, 307, 309–310
- Theory of Relativity, 61

Thermal conductivity
  affect of fouling factors on heat transfer, 439
  comparing transport property definitions, 475
  English Engineering units, 423
  handling multiple layers of, 427–429
  overview of, 422–423
  units of measure/conversion factors, 423
  of various materials, 423–424
Thermal equilibrium
  reversible vs. irreversible systems and, 143
  Zeroth Law of Thermodynamics for, 164–165
Thermal heat energy, 128–129
Thermodynamic efficiency (*eff*), 168–176
Thermodynamics
  activity and fugacity concepts in, 186–187
  adiabatic processes (compression/expansion), 167
  Carnot cycle and thermodynamic efficiency, 168–175
  concluding comments, 186
  conservation of energy and matter, 128–130
  divide and conquer in, 175–176
  enthalpy and internal energy, 135–138
  entropy, 139–142
  entropy of mixtures, 151–158
  First Law of Thermodynamics, 165–166
  free energy, chemical potential and entropy, 160–164
  functions of state, 144–145
  heat and its equivalence, 127–128
  heat capacity, 131–135
  heat pumps, 178–179
  Joule-Thomson effect, 179–180
  latent vs. sensible heat, 158–160
  Mollier diagram, 145–148
  nomenclature, 187–188
  power, 138–139
  problems/selected answers, 188–192, 538–539
  refrigeration, 176–178
  reversible vs. irreversible systems, 142–144
  Second Law of Thermodynamics, 166
  steam tables. *See* Steam tables
  systems, 182–185
  Third Law of Thermodynamics, 166–167
  turbo expanders, 181–182
  understanding, 123–126
  work, 130–131
  Zeroth Law of Thermodynamics, 164–165
Thin-film evaporators, 387
Third Law of Thermodynamics, 166–167
Third-order reactions, concentrations, 228–229
Three-step verbal communication, 6
Throttling process, Joule-Thomson, 179–180
Throughput, troubleshooting, 338
Time
  chemical reaction rates as function of, 229
  diffusion as function of, 482
  as fundamental unit of measure, 52
  Planck unit of, 140–141
  vs. temperature in phase transitions, 207
  as unit of measure, 53–54
Torque, measuring force, 66–68
Total mass, in material balance equations, 271
Total overhead condenser, distillation column, 509–514
Trailing zeroes with decimal point, significant figures, 84
Transient operations, steady-state vs., 273
Transport of momentum, velocity gradient for, 378
Transport phenomena
  fluid flow. *See* Fluid flow
  heat transfer. *See* Heat transfer
  mass transfer. *See* Mass transfer
Transport Phenomena (Bird et al.)
  Bernoulli equation applied to pipe flow of incompressible fluid, 409
  calculating area of sun and its view factor, 446
  on convection, 432
  equations of motion in, 392
  mass balance in, 472
  modeling mass transfer using theories in, 528
  omitting plots for mass-transfer coefficient, 520
  signage of heat-transfer process, 445
  and this book, 373
Tray-type absorbers, 484–485
Triangle
  calculating area of, 23–24, 33–36
  calculating volume of triangular prism, 30
Triple point of phase behavior, 205–206, 223
Troubleshooting
  throughput problems with energy balances, 338
  using material balances, 272–273
  using overall material balances, 262
Truncated cone, volume of, 44–45
Turbo-compounding, 175
Turbo-expanders, 181–182
Turbulence, increasing mass transfer, 483
Turbulent flow
  impossible to solve equations of motion for, 393
  overview, 384–385
  solving equations with Reynolds number, 396–401

U

U. See Internal energy
Ultraviolet (UV) light, 234–235
Underbars, in significant figures, 84
Unholy trinity of process problems, 337–338
Unit operations, defined, 17
  absorption, 484–488
  adsorption, 490–492
  distillation, 492–496
  liquid-liquid extraction, 496–497
  monitoring performance with material/energy balances, 498–502
  other processes, 497–498
  overview of, 469, 483
  in real world, 482–483
  stripping, 488–489
Unit Operations of Chemical Engineering (McCabe and Smith), 520
Unit operations, process technology
  chemical reactions of material, 19
  heating and/or cooling of material, 18
  movement of material, 18
  overview of, 17–18
  separations and purification of material, 19
United States Customary Units
  based on English units. *See* English (Imperial) units
  overview of, 52
Units of equilibrium, 194–195
Units of measure
  accuracy, precision, and variance, 80–84
  calculating answer to problem with, 11
  checking dimensional consistency of, 11
  concentrations, 72–75
  concluding comments, 88
  data input with, 10
  density and specific gravity, 68–69
  engineering accuracy and significant figures, 84–85
  heat conduction, 423
  length, 54–55
  mass, weight and force, 61–63
  mole unit, 69–72
  nomenclature, 88–89
  prefixes (M vs. m), 87–88
  pressure, 76–78
  problems/selected answers, 90–91, 538
  scientific notation, 85–86
  shear rate and viscosity, 379
  supplemental references, 89
  systems of, 51–52
  temperature, 56–61
  time, 53–54
  torque, moments, and couples, 66–68
  vectors, 63–66
  vernier scale, 86–87
  volume, 55–56
  work and power, 78–80
UV (ultraviolet) light, 234–235

V

V. See Volume
Vacuum, bubble point when boiling in, 200–201
van der Waals equation of state, 113–114
van der Waals forces
  causing clumping in laminar flow, 382
  equilibrium vapor pressure and, 196
  of free-flowing fluids, 375
  as induced dipoles, 109
  real gases and, 108
Vapor pressure
  effect of impurities on phase equilibrium, 209
  effect on boiling, 200–201
  equilibrium, 195–199
Vaporization
  energy balances of distillation column, 502–509
  latent heat of, 208
  as phase transition, 206–208
Vapor-liquid equilibrium, 193–194
Vapor-solid equilibrium, 194
Variable costs, business economics, 317
Variables
  calculating degrees of freedom, 12–16
  caution about less equations than, 15
  counting in problem solving, 8–9
  in material balances methodology, 267
Variance, as unit of measure, 80–84
Vector addition, 64
Vectors
  in fluid flow, 385–386
  in heat and mass transport, 374
  mass/heat transfers by diffusion as, 470
  measuring torque, moments, and couples for force, 66–68
  splitting into components, 385
  as unit of measure, 63–66
Velocity
  in dimensional analysis for fluid flow, 394–395
  effect on ethane cracking, 105–106
  HETP as function of, 527
  in laminar flow, 382–385
  measure of mass and rate of acceleration, 61–62
  shear rate and, 375
Velocity gradient, 376, 378

Velocity profiles, 374
Verbal communications, three steps of, 6
Vernier scale, 86–87
View factor, calculating area of sun and its, 446–448
Virga, 524
Viscosity
  comparing transport property definitions, 475
  HETP as function of, 527
  shear rate and, 375–382
Viscous drag, 375, 378
Viscous forces
  in fluid flow, 374, 376
  in laminar flow, 383–384
Volatility
  in distillation, 193, 492
  K values estimating, 213
Volume
  absolute temperature and, 97–98
  Boyle's Law and, 94–96
  calculating after batch blending, 288–289
  calculating concentrations using only, 289–290
  calculating degrees of freedom, 204
  calculating for 11.0 pounds of methane, 100–102
  calculating for ideal gas, 99–100
  change in relative, 104–105
  Charles's Law and, 96–97
  effect on equilibrium, 217–218
  of ethane, 115–118
  heat capacity at constant, 134–135
  internal energy and enthalpy, 135–138
  as unit of measure, 55–56
Volume, calculating
  complex objects, 36–40, 50
  concluding comments, 46
  cone, 32
  cube, 28–29
  cylinder, 30
  elliptical cylinder, 31
  overview of, 28
  problems/selected answers, 47–48, 50, 537–538
  rectangular prism, 29
  regular pyramid, 31
  sphere, 32
  spherical segment, 32–33
  triangular prism, 30
  truncated cone, 44–45
Volumetric flow rate, material balance, 280
Volumetric fractions, 110–111
Volumetric material balance, on distillation column, 276–278

W

W. See Work
Walls
  calculating volume of propane bullet tank, 38
  in convection, 431–433
  heat flow through containment, 343–344
  heat loss through composite, 427–430
  heat loss through distillation column, 349–350, 507
  heat-transfer flux in radiant section of process furnace, 444–445
  shell balance for fluid flowing through length of pipe, 456–458
  transport of heat through pipe/furnace, 420, 425–426
Water
  adding to boiler, 345–346
  calculating molar flux from falling raindrop, 522–524
  cooling hot oil with heat exchanger, 349
  dissolving ammonia gas into, 358–361
  heating in vessel to boiling point, 341–342
  heating to melt ice and produce steam, 340–341
  ion exchange in, 219–222
  laminar vs. turbulent flow, 382–385
  plotting enthalpy for steam, 211
Watt, James, 168
Watts
  as common units of power, 78
  equivalence of horsepower and, 79–80
Weight
  pressure caused by object exerting, 76–78
  as unit of measure, 61–63
  work and, 130
Width
  calculating areas of objects, 23–27
  calculating volumes of objects, 29–32
Work
  calculating, 130–131
  common units of, 78–80
  energy balances methodology, 338–340
  enthalpy, internal energy and, 135–138
  and entropy, 139–142
  mechanical equivalence between heat and, 127–128
  and power, 138–139

X

X-axis, 81–82
X direction, 375, 421, 473, 519, 529

Y

Y-axis, 389
Y direction, 423

Yield
  basing on limiting reactant, 306
  calculating chemical reactions, 240–243
  calculating fractional conversion from, 244–245
  chemical reaction/material balances and, 308–310
  of product from chemical reaction, 307–308

Z

Z-axis, 393
Z direction, 423, 473, 478
Zero (no) degrees of freedom, 14–15
Zero digits between nonzero digits, 84
Zero-order chemical reactions, 230
Zeroth Law of Thermodynamics
  material or energy balance in, 185
  overview of, 164–165
  radiation and, 443
Zones, process furnace, 420