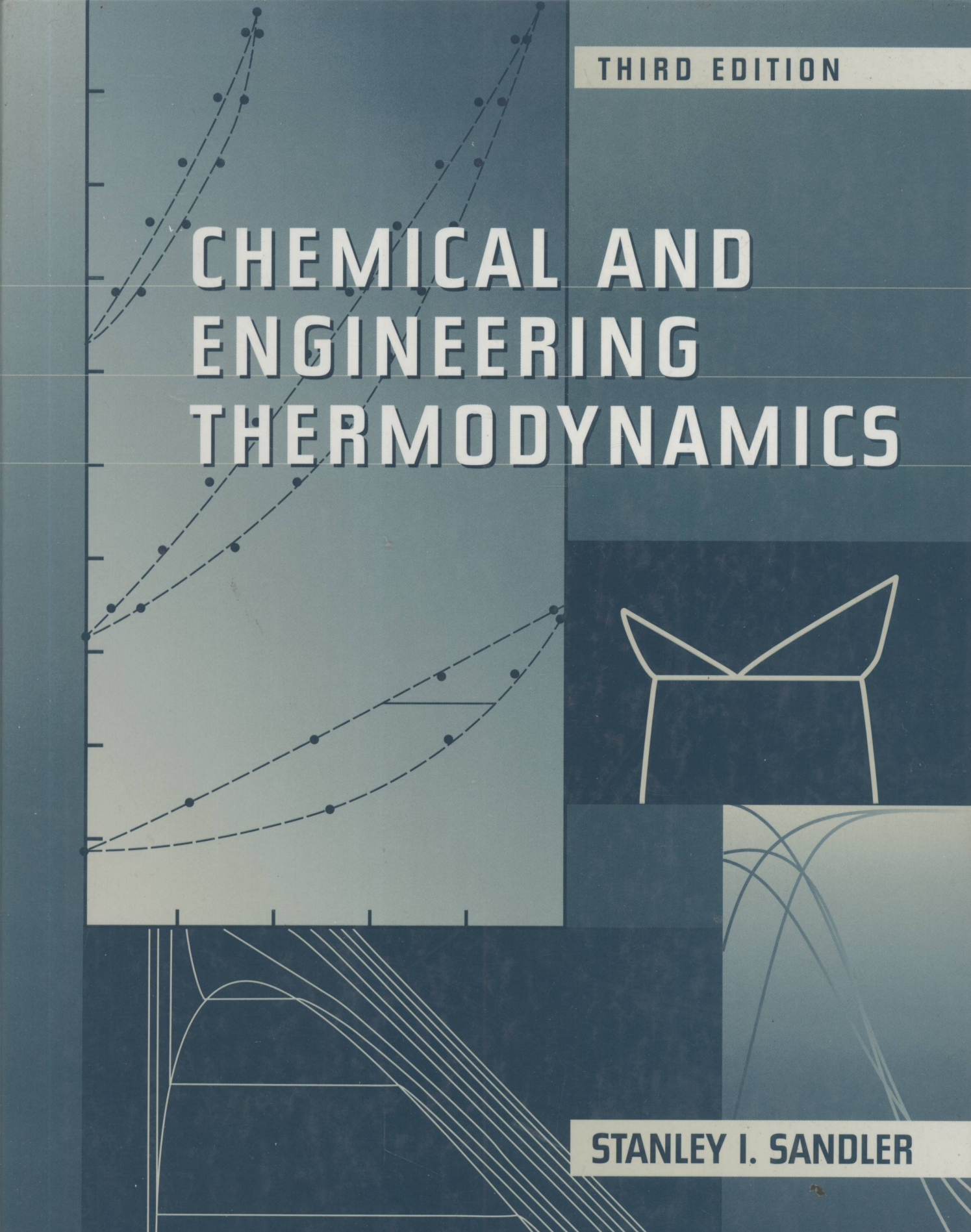




THIRD EDITION

# CHEMICAL AND ENGINEERING THERMODYNAMICS

STANLEY I. SANDLER

# Chemical and Engineering Thermodynamics

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Third Edition

**Stanley I. Sandler**  
*University of Delaware*



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# **Chemical and Engineering Thermodynamics**

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# Preface

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This book is intended to be the text for a course in thermodynamics for undergraduate students in chemical engineering. It has been used in this manner at the University of Delaware for more than twenty years, originally as a course for third-year students and currently for sophomores. I had two objectives in writing the first edition of this book, which have been retained in the succeeding editions. The first was to develop a modern applied thermodynamics text, especially for chemical engineering students, that was relevant to other parts of the curriculum, specifically courses in separations processes, chemical reactor analysis, and process design. The other objective was to organize and present material in sufficient detail, and in such a way that the student obtained a good understanding of the principles of thermodynamics, and a proficiency in applying these principles to the solution of a large variety of energy flow and equilibrium problems.

Since the first two editions largely met these goals, and the principles of thermodynamics have not changed in the last decade, this edition is similar in structure to the earlier ones. However, there have been three important changes in engineering education in the recent decades. The first is the availability of powerful desktop computers. The second is greater concerns about safety and the environment. The third is the application of chemical engineering principles to new technology areas such as biotechnology, polymers, solid-state processing, etc. In the current edition of this text I have made changes to address each of these issues.

The availability of desktop computers and equation-solving software has now made it possible to bring engineering science, industrial practice, and undergraduate education much closer together. In particular, students in their dormitory rooms or at home can now perform sophisticated thermodynamics and phase equilibrium calculations similar to those that they will encounter in industry. I provide two different ways to accomplish this.

The first is to utilize the set of programs I have developed for certain types of calculations. These programs are for: (1) the calculation of thermodynamic properties and vapor-liquid equilibrium of a pure fluid described by a cubic equation of state; (2) the calculation of the thermodynamic properties and phase equilibria for a multicomponent mixture described by a cubic equation of state; (3) the prediction of activity coefficients in a mixture using the UNIQUAC group contribution activity coefficient model; and (4) the calculation of chemical equilibrium constants and the standard state heats of reaction as a function of temperature using a database of

approximately 100 compounds. These programs are provided both as program code and as stand-alone executable modules.

The second is to make use of computer algebra/calculus programs such as MATHCAD®. The solutions to the illustrations and homework problems in this book were largely done with that program. Alternatively, students and instructors could use similar programs such as MATHEMATICA®, MAPLE®, MATLAB® or others. I believe that such computer algebra programs, that allow students to solve difficult problems without having to become experts in computer programming and numerical analysis, should have an important role throughout the chemical engineering curriculum. Most importantly, they let the student concentrate on the subject matter at hand, here thermodynamics, rather than being distracted by computational methods, algorithms and programming languages. However, while these equation-solving programs are valuable educational tools, there is nothing in this textbook that requires their use. This book can be used with or without such programs as the instructor feels is appropriate. For those who would like to explore the use of such programs, I have prepared a number of problem worksheets using MATHCAD®. The set of programs discussed above and the MATHCAD® worksheets can be downloaded from the Web site for this text. Access [www.wiley.com/college/sandler](http://www.wiley.com/college/sandler) and follow the instructions given there.

In an effort to make the subject of thermodynamics more accessible to the student I have made several pedagogical changes in this edition. First, the format of the book has been changed to provide room for marginal notes. The notes I have added are meant to emphasize the concepts I believe to be important, as well as to make it easier for the student to find those concepts again at a later time. Since I frequently write notes in the margins of books, I also wanted to provide a place for students to add notes of their own. A second change was to put boxes around important equations, so that the reader can easily identify the equations that are the end results of sometimes quite detailed analysis. In this way it is hoped that the student will easily see the important tree in what may appear to be a forest of equations. Also, I have provided a short title or description to indicate what is to be learned from or seen in each illustration.

A reader familiar with the second edition of this text will notice that while the basic structure of text is largely unchanged, there are many subtle changes. For example, SI units are now used throughout, and there are many new illustrative and homework problems. Illustrations have been added not only to demonstrate new concepts, but also to provide breaks among pages of mathematical derivations or thermodynamic philosophy. Also, to make thermodynamics and phase equilibria more relevant to the interests of students, I have added several new sections. One section deals with computing the distribution of a chemical pollutant throughout the environment as an illustration of multi-phase equilibria. Two other sections use thermodynamics to understand the dangers of physical and chemical explosions. There are also new sections introducing electrochemical processes, the phase behavior of polymer solutions, the thermodynamic behavior of molten metals, and coupled chemical reactions in biochemical systems. I have also added sections on traditional areas such as the liquefaction of gases, and on power and refrigeration cycles. Finally, I have included a section on the new class of mixing rules that combines equations of state and activity coefficient models. Such mixing rules are perhaps the most important development in applied thermodynamics in the last decade, and have greatly increased the range of applicability and utility of equations of state.

While some of the idiosyncrasies that appeared in the two earlier editions of this text remain here, the reader will find more use of the terms such as the first, second,

and third laws of thermodynamics, and chemical potential than I included in the earlier editions. I prefer, and continue to use, the partial molar Gibbs free energy, which describes the function exactly, to the traditional term of chemical potential. Likewise, I rather use the term energy balance than the first law, etc. Also, I prefer to show that the Carnot efficiency can easily be found once entropy is defined, rather than the more common procedure of introducing entropy (and the second law) in terms of the Carnot cycle. My experience with the latter method is that students have difficulty making the necessary generalization if the concept entropy and the second law are introduced in terms of a specific device.

It has been more than a decade since the appearance of the second edition of this book. During this time many people have encouraged me to prepare this third edition, and have graciously contributed their ideas and advice. The most important contributors have been the undergraduate and graduate students I have taught at Delaware with their incredibly inquisitive minds and penetrating questions. I have also benefited from the helpful comments of faculty colleagues at the University of Delaware and elsewhere who have used the earlier editions of this book. The comments of Professor Raul Lobo (Univ. of Delaware), who taught from a draft version of this third edition, and also contributed several new problems, and Professor Lawrence R. Dodd (Polytechnic Inst. of N.Y.), who has provided many corrections to the earlier edition, are greatly appreciated. Professor Clayton Radke (Univ. California–Berkeley) introduced me to the advantages of using MATHCAD® in undergraduate chemical engineering courses. The use of this tool in this edition is largely the result of the contagion of his enthusiasm that has spread to me. However, again I want to emphasize that there is nothing in this book that requires the use of MATHCAD® or any other equation-solving program.

Perhaps most important in completing this third edition was having the time available to do this. This was provided from several sources. First, and foremost my wife and (now grown) children, who over the years have graciously accepted the fact that I am so inefficient that I always work on evenings and weekends. Judith, my wife, has also proofread the galley proofs and helped prepare the index, and my son Michael has prepared some of the computer programs available on the Web site. Second, from the administration and my faculty colleagues at the University of Delaware who have provided the unencumbered time of a sabbatical leave that proved necessary for the completion of this revision. Finally, I also wish to thank my friends and colleagues in the Departments of Chemical Engineering at the University of California–Berkeley and the University of Queensland (Brisbane, Australia) for their hospitality, companionship and use of their facilities during that sabbatical leave.

*Stanley I. Sandler  
Newark, Delaware  
December 25, 1997*

*To Judith,  
Catherine,  
Joel,  
And Michael*

# About the Author

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STANLEY I. SANDLER earned the B.Ch.E. degree in 1962 from the City College of New York, and the Ph.D. in chemical engineering from the University of Minnesota in 1966. He was then a National Science Foundation Postdoctoral Fellow at the Institute for Molecular Physics at the University of Maryland for the 1966–67 academic year. He joined the faculty of the University of Delaware in 1967 as an assistant professor, and was promoted to associate professor in 1970, professor in 1973 and Henry Belin du Pont Professor of Chemical Engineering in 1982. He was department chairman from 1982 to 1986. He currently is also professor of chemistry and biochemistry at the University of Delaware and founding director of its Center for Molecular and Engineering Thermodynamics. He has been a visiting professor at Imperial College (London), the Technical University of Berlin, the University of Queensland (Australia) and the University of California, Berkeley.

In addition to this book, Professor Sandler is the author of 225 research papers and a monograph, and he is the editor of a book on thermodynamic modeling and five conference proceedings. Among his many awards and honors are a Faculty Scholar Award (1971) from the Camille and Henry Dreyfus Foundation, a Research Fellowship (1980) and U.S. Senior Scientist Award (1988) from the Alexander von Humboldt Foundation (Germany), the 3M Chemical Engineering Lectureship Award (1988) from the American Society for Engineering Education, the Professional Progress (1984) and Warren K. Lewis Awards (1996) from the American Institute of Chemical Engineers, the E. V. Murphree Award (1996) from the American Chemical Society, the Rossini Lectureship Award (1997) from the International Union of Pure and Applied Chemistry, and election to the U.S. National Academy of Engineering (1996).

# Contents

---

## NOTATION

xv

## CHAPTER 1

### INTRODUCTION

1

- 1.1 The Central Problems of Thermodynamics 1
  - 1.2 A System of Units 3
  - 1.3 The Equilibrium State 5
  - 1.4 Pressure, Temperature, and Equilibrium 7
  - 1.5 Heat, Work, and the Conservation of Energy 12
  - 1.6 Specification of the Equilibrium State; Intensive and Extensive Variables; Equations of State 15
  - 1.7 A Summary of Important Experimental Observations 18
  - 1.8 A Comment on the Development of Thermodynamics 20
- Problems 20

## CHAPTER 2

### CONSERVATION OF MASS AND ENERGY

22

- 2.1 A General Balance Equation and Conserved Quantities 23
  - 2.2 Conservation of Mass 27
  - 2.3 Conservation of Energy 30
  - 2.4 The Thermodynamic Properties of Matter 43
  - 2.5 Applications of the Mass and Energy Balances 51
  - 2.6 Conservation of Momentum 75
  - 2.7 The Microscopic Equations of Change for Thermodynamics and Fluid Mechanics (Optional) 76
- Problems 82

## CHAPTER 3

### ENTROPY: AN ADDITIONAL BALANCE EQUATION

89

- 3.1 Entropy: A New Concept 90
- 3.2 The Entropy Balance and Reversibility 97
- 3.3 Heat, Work, Engines, and Entropy 103
- 3.4 Entropy Changes of Matter 112
- 3.5 Applications of the Entropy Balance 115
- 3.6 Liquefaction 128

|                                                 |     |
|-------------------------------------------------|-----|
| 3.7 Power Generation and Refrigeration Cycles   | 132 |
| 3.8 The Thermodynamics of Mechanical Explosions | 154 |
| 3.9 The Microscopic Entropy Balance (Optional)  | 163 |
| Problems                                        | 165 |

## CHAPTER 4 THE THERMODYNAMIC PROPERTIES OF REAL SUBSTANCES 175

|                                                                                                                        |     |
|------------------------------------------------------------------------------------------------------------------------|-----|
| 4.1 Some Mathematical Preliminaries                                                                                    | 175 |
| 4.2 The Evaluation of Thermodynamic Partial Derivatives                                                                | 179 |
| 4.3 The Ideal Gas and Absolute-Temperature Scales                                                                      | 194 |
| 4.4 The Evaluation of Changes in the Thermodynamic Properties of Real Substances Accompanying a Change of State        | 195 |
| 4.5 An Example Involving the Change of State of a Real Gas                                                             | 219 |
| 4.6 The Principle of Corresponding States                                                                              | 225 |
| 4.7 Generalized Equations of State                                                                                     | 238 |
| 4.8 The Third Law of Thermodynamics                                                                                    | 242 |
| 4.9 More About Thermodynamic Partial Derivatives (Optional)                                                            | 243 |
| Appendix A4.1 A Program for Thermodynamic Properties Calculations Using the Peng-Robinson Cubic Equation of State, PR1 | 249 |
| Problems                                                                                                               | 251 |

## CHAPTER 5 EQUILIBRIUM AND STABILITY IN ONE-COMPONENT SYSTEMS 260

|                                                                                                                                             |     |
|---------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.1 The Criteria for Equilibrium                                                                                                            | 260 |
| 5.2 Stability of Thermodynamic Systems                                                                                                      | 265 |
| 5.3 Phase Equilibria: Application of the Equilibrium and Stability Criteria to the Equation of State                                        | 272 |
| 5.4 The Molar Gibbs Free Energy and Fugacity of a Pure Component                                                                            | 279 |
| 5.5 The Calculation of Pure Fluid-Phase Equilibrium: The Computation of Vapor Pressure from an Equation of State                            | 295 |
| 5.6 The Specification of the Equilibrium Thermodynamic State of a System of Several Phases: The Gibbs Phase Rule for a One-Component System | 303 |
| 5.7 Thermodynamic Properties of Phase Transitions                                                                                           | 307 |
| Problems                                                                                                                                    | 313 |

## CHAPTER 6 THE THERMODYNAMICS OF MULTICOMPONENT MIXTURES 324

|                                                                                  |     |
|----------------------------------------------------------------------------------|-----|
| 6.1 The Thermodynamic Description of Mixtures                                    | 324 |
| 6.2 The Partial Molar Gibbs Free Energy and the Generalized Gibbs-Duhem Equation | 333 |
| 6.3 A Notation for Chemical Reactions                                            | 337 |
| 6.4 The Equations of Change for a Multicomponent System                          | 340 |

|      |                                                                                                                       |     |
|------|-----------------------------------------------------------------------------------------------------------------------|-----|
| 6.5  | The Heat of Reaction and a Convention for the Thermodynamic Properties of Reacting Mixtures                           | 349 |
| 6.6  | The Experimental Determination of the Partial Molar Volume and Enthalpy                                               | 354 |
| 6.7  | Criteria for Phase Equilibrium in Multicomponent Systems                                                              | 364 |
| 6.8  | The Criteria for Chemical Equilibrium, and Combined Chemical and Phase Equilibrium                                    | 368 |
| 6.9  | The Specification of the Equilibrium Thermodynamic State of a Multicomponent, Multiphase System; the Gibbs Phase Rule | 373 |
| 6.10 | Some Concluding Remarks                                                                                               | 377 |
|      | Problems                                                                                                              | 377 |

**CHAPTER 7****THE ESTIMATION OF THE GIBBS FREE ENERGY AND FUGACITY OF A COMPONENT IN A MIXTURE****388**

|               |                                                                                                                                 |     |
|---------------|---------------------------------------------------------------------------------------------------------------------------------|-----|
| 7.1           | The Ideal Gas Mixture                                                                                                           | 388 |
| 7.2           | The Partial Molar Gibbs Free Energy and Fugacity                                                                                | 392 |
| 7.3           | The Ideal Mixture and Excess Mixture Properties                                                                                 | 396 |
| 7.4           | The Fugacity of Species in Gaseous, Liquid, and Solid Mixtures                                                                  | 406 |
| 7.5           | Several Correlative Liquid Mixture (Activity Coefficient) Models                                                                | 414 |
| 7.6           | Two Predictive Activity Coefficient Models                                                                                      | 428 |
| 7.7           | A Corresponding States Principle for Mixtures; The Pseudocritical Constant Method                                               | 437 |
| 7.8           | The Fugacity of Species in Nonsimple Mixtures                                                                                   | 444 |
| 7.9           | Some Comments on Reference and Standard States                                                                                  | 451 |
| 7.10          | A Combined Equation-of-State—Excess Gibbs Free Energy Models                                                                    | 452 |
| 7.11          | Electrolyte Solutions                                                                                                           | 455 |
| 7.12          | Concluding Remarks                                                                                                              | 461 |
| Appendix A7.1 | A Statistical Mechanical Interpretation of the Entropy of Mixing in an Ideal Mixture                                            | 464 |
| Appendix A7.2 | A Program for Multicomponent Vapor-Liquid Equilibrium Calculations Using the Peng-Robinson Cubic Equation of State, VLMU        | 467 |
| Appendix A7.3 | Multicomponent Excess Gibbs Free Energy (Activity Coefficient) Models                                                           | 468 |
| Appendix A7.4 | A Program for the Prediction of Activity Coefficients and Low Pressure Vapor-Liquid Equilibrium Using the UNIFAC Model, UNIFAC. | 470 |
|               | Problems                                                                                                                        | 471 |

**CHAPTER 8****PHASE EQUILIBRIUM IN MIXTURES****478**

|     |                                                           |     |
|-----|-----------------------------------------------------------|-----|
| 8.1 | Vapor-Liquid Equilibria Using Activity Coefficient Models | 478 |
|     | Problems for Section 8.1                                  | 511 |
| 8.2 | Vapor-Liquid Equilibria Using Equations of State          | 518 |
|     | Problems for Section 8.2                                  | 534 |
| 8.3 | The Solubility of a Gas in a Liquid                       | 536 |

|                                                                                                                   |     |
|-------------------------------------------------------------------------------------------------------------------|-----|
| Problems for Section 8.3                                                                                          | 547 |
| 8.4 The Solubility of a Liquid in a Liquid and Vapor-Liquid-Liquid Equilibrium                                    | 550 |
| Problems for Section 8.4                                                                                          | 571 |
| 8.5 The Solubility of a Solid in a Liquid, Gas, or Supercritical Fluid                                            | 575 |
| Problems for Section 8.5                                                                                          | 585 |
| 8.6 The Partitioning of a Solute Among Two Coexisting Liquid Phases; The Distribution Coefficient                 | 586 |
| Problems for Section 8.6                                                                                          | 597 |
| 8.7 Freezing-Point Depression of a Solvent Due to the Presence of a Solute; the Freezing Point of Liquid Mixtures | 598 |
| Problems for Section 8.7                                                                                          | 602 |
| 8.8 Osmotic Equilibrium and Osmotic Pressure                                                                      | 603 |
| Problems for Section 8.8                                                                                          | 606 |
| 8.9 The Phase Behavior Modeling of Chemicals in the Environment                                                   | 608 |
| Problems for Section 8.9                                                                                          | 613 |
| 8.10 The Phase Behavior of Solid Mixtures                                                                         | 614 |
| Problems for Section 8.10                                                                                         | 622 |
| 8.11 Concluding Remarks                                                                                           | 623 |
| Additional Phase Equilibrium Problems                                                                             | 624 |

## CHAPTER 9

### CHEMICAL EQUILIBRIUM AND THE BALANCE EQUATIONS FOR CHEMICALLY REACTING SYSTEMS

630

|                                                                                                                    |     |
|--------------------------------------------------------------------------------------------------------------------|-----|
| 9.1 Chemical Equilibrium in a Single-Phase System                                                                  | 630 |
| 9.2 Heterogeneous Chemical Reactions                                                                               | 663 |
| 9.3 Chemical Equilibrium When Several Reactions Occur in a Single Phase                                            | 676 |
| 9.4 Combined Chemical and Phase Equilibrium                                                                        | 683 |
| 9.5 The Balance Equations for a Tank-Type Chemical Reactor                                                         | 691 |
| 9.6 The Balance Equations for a Tubular Reactor                                                                    | 699 |
| 9.7 Overall Reactor Balance Equations and the Adiabatic Reaction Temperature                                       | 702 |
| 9.8 The Thermodynamics of Chemical Explosions                                                                      | 711 |
| 9.9 Introduction to Electrochemical Processes                                                                      | 717 |
| 9.10 Coupled Chemical Reactions                                                                                    | 727 |
| Appendix A9.1 A Program for the Calculation of Chemical Equilibrium Constants As a Function of Temperature, CHEMEQ | 730 |
| Problems                                                                                                           | 731 |

## APPENDIXES

744

|                                                                                       |     |
|---------------------------------------------------------------------------------------|-----|
| Appendix I Conversion Factors for SI Units                                            | 744 |
| Appendix II The Molar Heat Capacities of Gases in the Ideal Gas (Zero Pressure) State | 745 |
| Appendix III The Thermodynamic Properties of Water and Steam                          | 748 |
| Appendix IV Enthalpies and Free Energies of Formation                                 | 758 |
| Appendix V Heats of Combustion                                                        | 761 |

## INDEX

763

# Notation

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Standard, generally accepted notation has been used throughout this text. This list contains the important symbols, their definition, and, when appropriate, the page of first occurrence (where a more detailed definition is given). Symbols used only once, or within only a single section are not listed. In a few cases it has been necessary to use the same symbol twice. These occurrences are rare and widely separated, so it is hoped no confusion will result.

## SPECIAL NOTATION

| Symbol                                                        | Designates                                                                                                     |
|---------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| $\hat{\phantom{x}}$ (caret as in $\hat{H}$ )                  | property per unit mass (enthalpy per unit mass)                                                                |
| $\underline{\phantom{x}}$ (underscore as in $\underline{H}$ ) | property per mole (enthalpy per mole)                                                                          |
| $\bar{\phantom{x}}$ (overbar as in $\bar{H}_i$ )              | partial molar property (partial molar enthalpy)                                                                |
| $\pm$ (as in $M_{\pm}$ )                                      | mean ionic property (mean ionic molality)                                                                      |
| $*$ (as in $G_i^*$ )                                          | property (Gibbs free energy) in hypothetical pure component state extrapolated from infinite dilution behavior |
| $\square$ (as in $\bar{G}_i^{\square}$ )                      | ideal unit molal property (Gibbs free energy) extrapolated from infinite dilution behavior                     |
| $\circ$                                                       | standard state                                                                                                 |

## GENERAL NOTATION

| Symbol              | Designates                                                   |
|---------------------|--------------------------------------------------------------|
| $A$                 | Helmholtz free energy (100)                                  |
| $a_i$               | activity of species $i$ (637)                                |
| $a, b, c, \dots$    | constants in heat capacity equation, equation of state, etc. |
| $B(T), C(T), \dots$ | virial coefficients (197)                                    |
| $\mathcal{C}$       | number of components (324)                                   |
| $^{\circ}\text{C}$  | degrees Celsius (11)                                         |

| Symbol                                                                                                              | Designates                                                                                                |
|---------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|
| $C_i$                                                                                                               | concentration of species $i$ (588, 593)                                                                   |
| $C_V, C_P$                                                                                                          | constant-volume and constant-pressure heat capacities (44)                                                |
| $C_L$                                                                                                               | heat capacity at constant length (255)                                                                    |
| $C_V^*, C_P^*$                                                                                                      | ideal gas heat capacity (45)                                                                              |
| $\partial, d, D$                                                                                                    | partial, total, and substantial derivative symbols                                                        |
| $D$                                                                                                                 | diffusion coefficient (19)                                                                                |
| $\mathcal{F}$                                                                                                       | degrees of freedom (304)                                                                                  |
| $^{\circ}\text{F}$                                                                                                  | degrees Fahrenheit (11)                                                                                   |
| $f$                                                                                                                 | pure component fugacity (280)                                                                             |
| $\bar{f}_i$                                                                                                         | fugacity of a species in a mixture (391)                                                                  |
| $F_{\text{fr}}$                                                                                                     | frictional forces (67)                                                                                    |
| $g$                                                                                                                 | acceleration of gravity (8)                                                                               |
| $G$                                                                                                                 | Gibbs free energy (100)                                                                                   |
| $\Delta G^{\text{fus}}, \Delta G_{\text{rxn}}, \Delta G_{\text{mix}}$                                               | Gibbs free energy changes on fusion (576), reaction (351), and mixing (390)                               |
| $\Delta G_{f,i}^{\circ}$                                                                                            | molar Gibbs free energy of formation of species $i$ (350)                                                 |
| $H$                                                                                                                 | enthalpy (33)                                                                                             |
| $H_i, \mathcal{H}_i$                                                                                                | Henry's law constants (448, 449)                                                                          |
| $\Delta H^{\text{vap}}, \Delta H^{\text{fus}}, \Delta H^{\text{sub}}, \Delta H_{\text{mix}}, \Delta H_{\text{rxn}}$ | enthalpy changes on vaporization (308), fusion (311), sublimation (311), mixing (325), and reaction (350) |
| $\Delta H_{C,i}^{\circ}$                                                                                            | standard heat of combustion of species $i$ (352)                                                          |
| $\Delta H_{f,i}^{\circ}$                                                                                            | molar heat of formation of species $i$ (350)                                                              |
| $\Delta H_s$                                                                                                        | molar integral heat solution (380)                                                                        |
| $I$                                                                                                                 | ionic strength (458) in Chapters 7–9                                                                      |
| $\mathbf{I}$                                                                                                        | unit tensor (82)                                                                                          |
| $K$                                                                                                                 | number of flow streams (27)                                                                               |
| $K$                                                                                                                 | critical end point (521)                                                                                  |
| $K$                                                                                                                 | degrees Kelvin (11)                                                                                       |
| $K, K_c, K_x$                                                                                                       | distribution coefficients (495, 587, 588) in Chapter 8                                                    |
| $K_a$                                                                                                               | chemical equilibrium constant (639)                                                                       |
| $K_c, K_p, K_x, K_y$                                                                                                | chemical equilibrium ratios (651) in Chapter 9                                                            |
| $K_c^{\circ}, K_s^{\circ}$                                                                                          | ideal solution ionization (660) and solubility (669) products                                             |
| $k_{\text{fr}}$                                                                                                     | coefficient of sliding friction (68)                                                                      |
| $K_i$                                                                                                               | $K$ -factor, $y_i/x_i$ (494)                                                                              |
| $K_s$                                                                                                               | solubility product (668)                                                                                  |
| $K_{\gamma}$                                                                                                        | product of activity coefficients (652)                                                                    |
| $K_{\nu}$                                                                                                           | product of fugacity coefficients (652)                                                                    |
| $K_{\text{OW}}$                                                                                                     | octanol-water position coefficient (593)                                                                  |

|                                                  |                                                                                   |
|--------------------------------------------------|-----------------------------------------------------------------------------------|
| $L$                                              | moles of liquid phase (493)                                                       |
| $L$                                              | lower critical end point (521)                                                    |
| $M$                                              | mass (8)                                                                          |
| $\dot{M}$                                        | mass flow rate (27)                                                               |
| $m$                                              | molecular weight (27)                                                             |
| $\mathcal{M}$                                    | number of independent chemical reactions (340)                                    |
| $\Delta M_k$                                     | amount of mass that entered from $k$ th flow stream (28)                          |
| $M_1$                                            | mass of system in state 1 (28) or mass of species 1 (342)                         |
| $M$                                              | melting point (521)                                                               |
| $N$                                              | number of moles (27)                                                              |
| $N_{i,0}$                                        | initial number of moles of species $i$ (340)                                      |
| $P$                                              | pressure (9)                                                                      |
| $\mathbf{P}$                                     | pressure tensor (80)                                                              |
| $\mathcal{P}$                                    | number of phases (303)                                                            |
| $P^{\text{vap}}, P^{\text{sub}}, P^{\text{sat}}$ | vapor (308), sublimation (308), and saturation pressures (308)                    |
| $P_{\text{atm}}$                                 | atmospheric pressure (9)                                                          |
| $P_C, P_{C,m}$                                   | critical pressure (226) and mixture pseudocritical pressure (439)                 |
| $P_T$                                            | triple point pressure (277)                                                       |
| $P_g$                                            | gauge pressure (8)                                                                |
| $P_i$                                            | partial pressure of species $i$ (480)                                             |
| $P_r, P_{r,m}$                                   | reduced pressure for a pure component (229) and a mixture (439)                   |
| $P_{\text{rxn}}$                                 | reaction pressure (647)                                                           |
| $Q, \dot{Q}$                                     | heat flow (19) and heat flow rate (30)                                            |
| $\mathbf{q}$                                     | heat flux vector (80)                                                             |
| $q$                                              | volumetric flow rate (691)                                                        |
| $R$                                              | gas constant (10)                                                                 |
| $r$                                              | specific reaction rate (340)                                                      |
| $S$                                              | entropy (91)                                                                      |
| $S_{\text{gen}}, \dot{S}_{\text{gen}}$           | entropy generated (93) and entropy generation rate (91)                           |
| $S_{UV}, S_{UN}, \text{etc.}$                    | second partial derivatives of entropy (266)                                       |
| $T$                                              | temperature (10)                                                                  |
| $T_C, T_{C,m}$                                   | critical temperature (226) and mixture pseudocritical temperature (439)           |
| $T_f$                                            | mixture freezing temperature (598)                                                |
| $T_{lc}, T_{uc}$                                 | lower and upper consolute temperatures (557)                                      |
| $T_m$                                            | melting temperature (575)                                                         |
| $T_r, T_{r,m}$                                   | reduced temperature of a pure fluid (229) and a mixture (439)                     |
| $T_T$                                            | triple point temperature (277, 577)                                               |
| $U$                                              | internal energy and mixture internal energy (324)                                 |
| $V$                                              | volume (10), mixture volume (324) (also moles of vapor in Secs. 8.1 and 9.4 only) |

| Symbol                                   | Designates                                                                                 |
|------------------------------------------|--------------------------------------------------------------------------------------------|
| $\Delta V^{\text{fus}}$                  | volume change on melting or fusion (578)                                                   |
| $v$                                      | velocity (20)                                                                              |
| $v_s$                                    | velocity of sound (255)                                                                    |
| $\mathbf{v}$                             | velocity vector (80)                                                                       |
| $V_C$                                    | molar critical volume (226)                                                                |
| $\Delta V_{\text{mix}}$                  | volume change on mixing (325)                                                              |
| $V_r$                                    | reduced volume (229)                                                                       |
| $w_i$                                    | mass fraction (325)                                                                        |
| $W, \dot{W}$                             | work (31) and rate at which work is supplied to system (31)                                |
| $W^{\text{NET}}$                         | net work supplied from surroundings (70)                                                   |
| $W_{\text{fr}}$                          | work against friction (70)                                                                 |
| $W_s, \dot{W}_s$                         | shaft work (30) and rate of shaft work (30)                                                |
| $X$                                      | any thermodynamic variable in Chapter 4, molar extent of chemical reaction (337) elsewhere |
| $x$                                      | coordinate direction                                                                       |
| $x^{\text{I}}, x^{\text{II}}$            | fraction of mass in a phase (50)                                                           |
| $x^{\text{L}}, x^{\text{V}}$             | fraction of mass in vapor and liquid phases (274)                                          |
| $x_i$                                    | mole fraction of species $i$ in vapor or liquid phase (325)                                |
| $Y$                                      | any thermodynamic variable (176)                                                           |
| $y$                                      | coordinate direction                                                                       |
| $y_i$                                    | vapor-phase mole fraction (406)                                                            |
| $Z, Z_m$                                 | compressibility factor of a pure fluid (197) and a mixture (435)                           |
| $z$                                      | coordinate direction                                                                       |
| $Z_C$                                    | critical compressibility (227)                                                             |
| $z_+, z_-$                               | ionic valence (456)                                                                        |
| $\alpha$                                 | coefficient of thermal expansion (179) (in Chapter 4)                                      |
| $\alpha, \beta$                          | coefficients in van Laar and Debye-Hückel equations (Chapters 7–9)                         |
| $\gamma$                                 | specific heat ratio (65)                                                                   |
| $\gamma_i, \gamma_i^*, \gamma_i^\square$ | activity coefficients of species $i$ (399, 448, 449)                                       |
| $\gamma_\pm$                             | mean ionic activity coefficient (457)                                                      |
| $\delta$                                 | solubility parameter (431)                                                                 |
| $\delta_{ij}$                            | Kronecker delta function (164)                                                             |
| $\theta$                                 | general thermodynamic variable (26, 50)                                                    |
| $\kappa_S$                               | adiabatic compressibility (251)                                                            |
| $\kappa_T$                               | isothermal compressibility (179)                                                           |
| $\mu$                                    | viscosity (20), Joule-Thomson coefficient (185), chemical potential (367)                  |
| $\nu$                                    | stoichiometric coefficient (337)                                                           |
| $\nu_+, \nu_-$                           | ionic stoichiometric coefficient (456)                                                     |