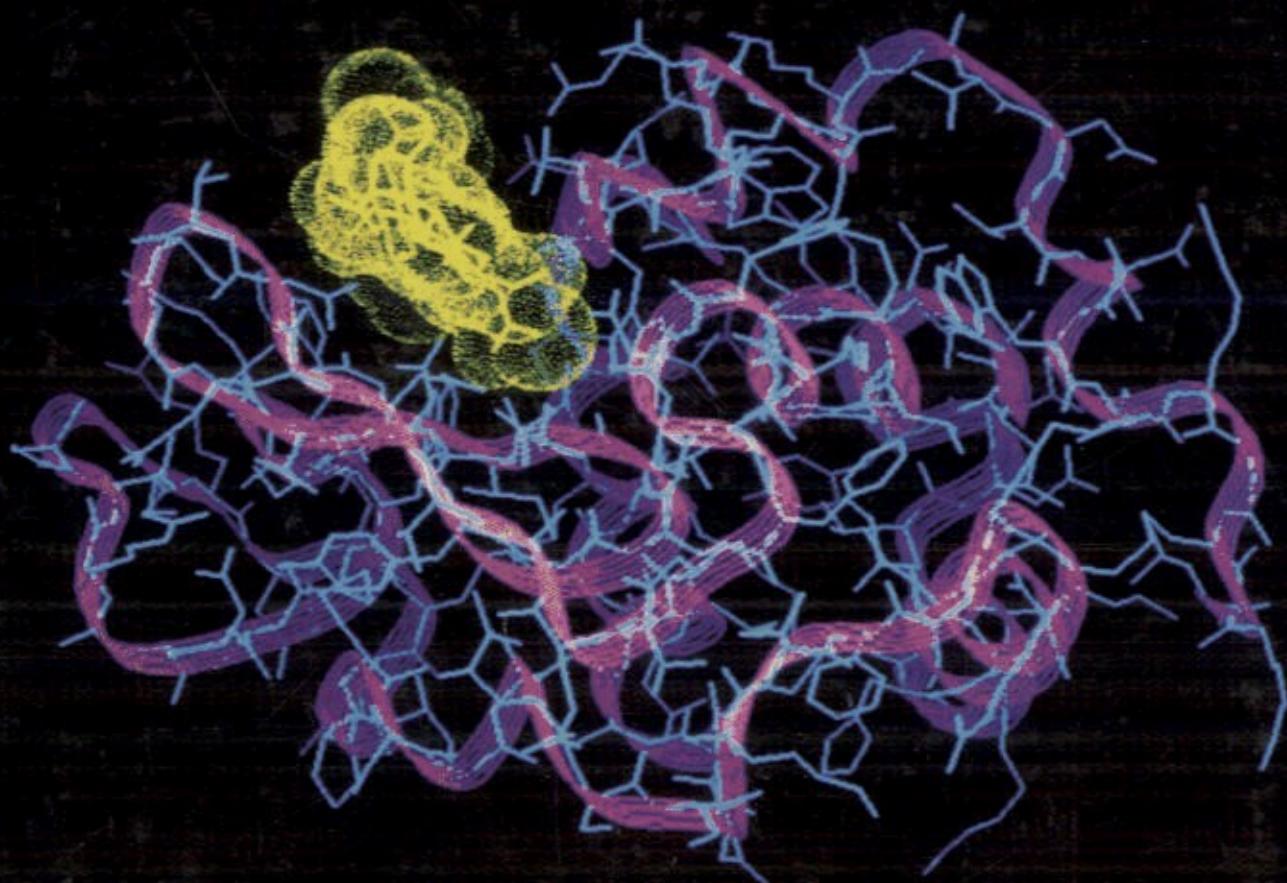
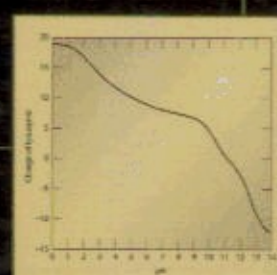
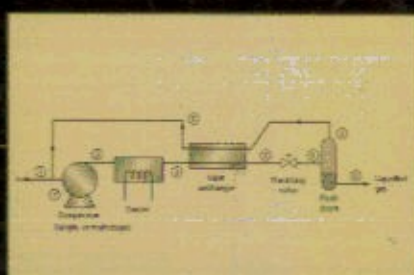
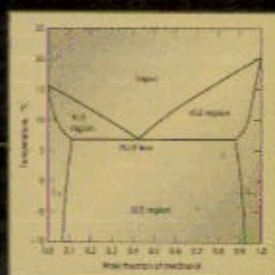


Chemical, Biochemical, and Engineering Thermodynamics

STANLEY I. SANDLER

4E



Contents

CHAPTER 1	INTRODUCTION	1
	1.1 The Central Problems of Thermodynamics	4
	1.2 A System of Units	5
	1.3 The Equilibrium State	7
	1.4 Pressure, Temperature, and Equilibrium	10
	1.5 Heat, Work, and the Conservation of Energy	15
	1.6 Specification of the Equilibrium State; Intensive and Extensive Variables; Equations of State	18
	1.7 A Summary of Important Experimental Observations	21
	1.8 A Comment on the Development of Thermodynamics	23
	Problems	23
CHAPTER 2	CONSERVATION OF MASS	25
	2.1 A General Balance Equation and Conserved Quantities	26
	2.2 Conservation of Mass	30
	2.3 The Mass Balance Equations for a Multicomponent System with a Chemical Reaction	35
	2.4 The Microscopic Mass Balance Equations in Thermodynamics and Fluid Mechanics (Optional) (CD only)	
	Problems	44
CHAPTER 3	CONSERVATION OF ENERGY	45
	3.1 Conservation of Energy	47
	3.2 Several Examples of Using the Energy Balance	54
	3.3 The Thermodynamic Properties of Matter	59
	3.4 Applications of the Mass and Energy Balances	69
	3.5 Conservation of Momentum	92
	3.6 The Microscopic Energy Balance (Optional) (CD only)	
	Problems	93
CHAPTER 4	ENTROPY: AN ADDITIONAL BALANCE EQUATION	98
	4.1 Entropy: A New Concept	99
	4.2 The Entropy Balance and Reversibility	107
	4.3 Heat, Work, Engines, and Entropy	113
	4.4 Entropy Changes of Matter	124
	4.5 Applications of the Entropy Balance	127
	4.6 The Microscopic Entropy Balance (Optional) (CD only)	
	Problems	139
CHAPTER 5	LIQUEFACTION, POWER CYCLES, AND EXPLOSIONS	147
	5.1 Liquefaction	147
	5.2 Power Generation and Refrigeration Cycles	152
	5.3 The Thermodynamics of Mechanical Explosions	173
	Problems	182
CHAPTER 6	THE THERMODYNAMIC PROPERTIES OF REAL SUBSTANCES	187
	6.1 Some Mathematical Preliminaries	188
	6.2 The Evaluation of Thermodynamic Partial Derivatives	192

	6.3 The Ideal Gas and Absolute Temperature Scales	206
	6.4 The Evaluation of Changes in the Thermodynamic Properties of Real Substances Accompanying a Change of State	207
	6.5 An Example Involving the Change of State of a Real Gas	232
	6.6 The Principle of Corresponding States	237
	6.7 Generalized Equations of State	250
	6.8 The Third Law of Thermodynamics	254
	6.9 Estimation Methods for Critical and Other Properties	255
	6.10 More About Thermodynamic Partial Derivatives (Optional) (CD only)	
	Problems	259
CHAPTER 7	EQUILIBRIUM AND STABILITY IN ONE-COMPONENT SYSTEMS	268
	7.1 The Criteria for Equilibrium	269
	7.2 Stability of Thermodynamic Systems	276
	7.3 Phase Equilibria: Application of the Equilibrium and Stability Criteria to the Equation of State	283
	7.4 The Molar Gibbs Energy and Fugacity of a Pure Component	290
	7.5 The Calculation of Pure Fluid-Phase Equilibrium: The Computation of Vapor Pressure from an Equation of State	305
	7.6 Specification of the Equilibrium Thermodynamic State of a System of Several Phases: The Gibbs Phase Rule for a One-Component System	313
	7.7 Thermodynamic Properties of Phase Transitions	317
	7.8 Thermodynamic Properties of Small Systems, or Why Subcooling and Superheating Occur	324
	Problems	327
CHAPTER 8	THE THERMODYNAMICS OF MULTICOMPONENT MIXTURES	336
	8.1 The Thermodynamic Description of Mixtures	337
	8.2 The Partial Molar Gibbs Energy and the Generalized Gibbs-Duhem Equation	346
	8.3 A Notation for Chemical Reactions	350
	8.4 The Equations of Change for a Multicomponent System	353
	8.5 The Heat of Reaction and a Convention for the Thermodynamic Properties of Reacting Mixtures	361
	8.6 The Experimental Determination of the Partial Molar Volume and Enthalpy	368
	8.7 Criteria for Phase Equilibrium in Multicomponent Systems	378
	8.8 Criteria for Chemical Equilibrium, and Combined Chemical and Phase Equilibrium	382
	8.9 Specification of the Equilibrium Thermodynamic State of a Multicomponent, Multiphase System; the Gibbs Phase Rule	387
	8.10 A Concluding Remark	391
	Problems	391
CHAPTER 9	ESTIMATION OF THE GIBBS ENERGY AND FUGACITY OF A COMPONENT IN A MIXTURE	399
	9.1 The Ideal Gas Mixture	400
	9.2 The Partial Molar Gibbs Energy and Fugacity	404
	9.3 Ideal Mixture and Excess Mixture Properties	408
	9.4 Fugacity of Species in Gaseous, Liquid, and Solid Mixtures	419
	9.5 Several Correlative Liquid Mixture Activity Coefficient Models	429
	9.6 Two Predictive Activity Coefficient Models	443

	9.7 Fugacity of Species in Nonsimple Mixtures	451
	9.8 Some Comments on Reference and Standard States	461
	9.9 Combined Equation-of-State and Excess Gibbs Energy Model	462
	9.10 Electrolyte Solutions	465
	9.11 Choosing the Appropriate Thermodynamic Model	473
	Appendix 9.1 A Statistical Mechanical Interpretation of the Entropy of Mixing in an Ideal Mixture (CD only)	476
	Appendix 9.2 Multicomponent Excess Gibbs Energy (Activity Coefficient) Models	476
	Appendix 9.3 The Activity Coefficient of a Solvent in an Electrolyte Solution	478
	Problems	482
CHAPTER 10	VAPOR-LIQUID EQUILIBRIUM IN MIXTURES	489
	10.0 Introduction to Vapor-Liquid Equilibrium	490
	10.1 Vapor-Liquid Equilibrium in Ideal Mixtures	492
	Problems for Section 10.1	518
	10.2 Low-Pressure Vapor-Liquid Equilibrium in Nonideal Mixtures	519
	Problems for Section 10.2	548
	10.3 High-Pressure Vapor-Liquid Equilibria Using Equations of State (ϕ - ϕ Method)	556
	Problems for Section 10.3	572
CHAPTER 11	OTHER TYPES OF PHASE EQUILIBRIA IN FLUID MIXTURES	575
	11.1 The Solubility of a Gas in a Liquid	576
	Problems for Section 11.1	591
	11.2 Liquid-Liquid Equilibrium	593
	Problems for Section 11.2	621
	11.3 Vapor-Liquid-Liquid Equilibrium	625
	Problems for Section 11.3	633
	11.4 The Partitioning of a Solute Among Two Coexisting Liquid Phases; The Distribution Coefficient	636
	Problems for Section 11.4	646
	11.5 Osmotic Equilibrium and Osmotic Pressure	648
	Problems for Section 11.5	655
CHAPTER 12	MIXTURE PHASE EQUILIBRIA INVOLVING SOLIDS	658
	12.1 The Solubility of a Solid in a Liquid, Gas, or Supercritical Fluid	659
	Problems for Section 12.1	669
	12.2 Partitioning of a Solid Solute Between Two Liquid Phases	670
	Problem for Section 12.2	673
	12.3 Freezing-Point Depression of a Solvent Due to the Presence of a Solute; the Freezing Point of Liquid Mixtures	673
	Problems for Section 12.3	678
	12.4 Phase Behavior of Solid Mixtures	679
	Problems for Section 12.4	687
	12.5 The Phase Behavior Modeling of Chemicals in the Environment	689
	Problems for Section 12.5	695
	12.6 Process Design and Product Design	695
	Problem for Section 12.6	701
	12.7 Concluding Remarks on Phase Equilibria	701

CHAPTER 13	CHEMICAL EQUILIBRIUM	703
	13.1 Chemical Equilibrium in a Single-Phase System	704
	13.2 Heterogeneous Chemical Reactions	737
	13.3 Chemical Equilibrium When Several Reactions Occur in a Single Phase	750
	13.4 Combined Chemical and Phase Equilibrium	760
	Problems	767
CHAPTER 14	THE BALANCE EQUATIONS FOR CHEMICAL REACTORS AND ELECTROCHEMISTRY	778
	14.1 The Balance Equations for a Tank-Type Chemical Reactor	779
	14.2 The Balance Equations for a Tubular Reactor	787
	14.3 Overall Reactor Balance Equations and the Adiabatic Reaction Temperature	791
	14.4 Thermodynamics of Chemical Explosions	799
	14.5 Availability and Available Work in Chemically Reacting Systems	805
	14.6 Introduction to Electrochemical Processes	810
	Problems	819
CHAPTER 15	SOME BIOCHEMICAL APPLICATIONS OF THERMODYNAMICS	822
	15.1 Acidity of Solutions	823
	15.2 Ionization of Biochemicals	841
	15.3 Solubilities of Weak Acids, Weak Bases, and Pharmaceuticals as a Function of pH	851
	15.4 Binding of a Ligand to a Substrate	858
	15.5 Some Other Examples of Biochemical Reactions	863
	15.6 Protein Concentration in an Ultracentrifuge	870
	15.7 Gibbs-Donnan Equilibrium and Membrane Potentials	873
	15.8 Coupled Chemical Reactions: the ATP-ADP Energy Storage and Delivery Mechanism	880
	15.9 Thermodynamic Analysis of Fermenters and Other Bioreactors	885
	Problems	908
APPENDICES		913
	Appendix A.I Conversion Factors to SI Units	913
	Appendix A.II The Molar Heat Capacities of Gases in the Ideal Gas (Zero-Pressure) State	914
	Appendix A.III The Thermodynamic Properties of Water and Steam	917
	Appendix A.IV Enthalpies and Gibbs Energies of Formation	927
	Appendix A.V Heats of Combustion	930
	Appendix B Brief Descriptions of Computer Programs and Computer Aids for Use with This Book	931
	Appendix B Descriptions of Computer Programs and Computer Aids for Use with This Book (CD only)	CDB1
	B.I Windows-Based Visual Basic Programs	CDB1
	B.II DOS-Based Basic Programs	CDB9
	B.III MATHCAD Worksheets	CDB12
	B.IV MATLAB Programs	CDB14
	Appendix C Answers to Selected Problems	933
INDEX		936