

# Contents

<b>List of Symbols</b>	viii
<b>Preface</b>	xiii
<b>1 INTRODUCTION</b>	1
1.1 The Scope of Thermodynamics . . . . .	1
1.2 International System of Units . . . . .	4
1.3 Measures of Amount or Size . . . . .	6
1.4 Temperature . . . . .	7
1.5 Pressure . . . . .	8
1.6 Work . . . . .	10
1.7 Energy . . . . .	11
1.8 Heat . . . . .	16
1.9 Synopsis . . . . .	17
1.10 Problems . . . . .	18
<b>2 THE FIRST LAW AND OTHER BASIC CONCEPTS</b>	24
2.1 Joule's Experiments . . . . .	24
2.2 Internal Energy . . . . .	25
2.3 The First Law of Thermodynamics . . . . .	25
2.4 Energy Balance for Closed Systems . . . . .	26
2.5 Equilibrium and the Thermodynamic State . . . . .	30
2.6 The Reversible Process . . . . .	35
2.7 Closed-System Reversible Processes; Enthalpy . . . . .	39
2.8 Heat Capacity . . . . .	42
2.9 Mass and Energy Balances for Open Systems . . . . .	47
2.10 Synopsis . . . . .	59
2.11 Problems . . . . .	59
<b>3 VOLUMETRIC PROPERTIES OF PURE FLUIDS</b>	68
3.1 The Phase Rule . . . . .	68
3.2 PVT Behavior of Pure Substances . . . . .	70
3.3 Ideal Gas and Ideal-Gas State . . . . .	77
3.4 Virial Equations of State . . . . .	89

<b>3.5</b>	Application of the Virial Equations . . . . .	92
<b>3.6</b>	Cubic Equations of State . . . . .	95
<b>3.7</b>	Generalized Correlations for Gases . . . . .	103
<b>3.8</b>	Generalized Correlations for Liquids . . . . .	112
<b>3.9</b>	Synopsis . . . . .	115
<b>3.10</b>	Problems. . . . .	116
<b>4</b>	<b>HEAT EFFECTS</b>	<b>133</b>
<b>4.1</b>	Sensible Heat Effects . . . . .	134
<b>4.2</b>	Latent Heats of Pure Substances . . . . .	141
<b>4.3</b>	Standard Heat of Reaction . . . . .	144
<b>4.4</b>	Standard Heat of Formation . . . . .	146
<b>4.5</b>	Standard Heat of Combustion . . . . .	148
<b>4.6</b>	Temperature Dependence of $\Delta H^\circ$ . . . . .	149
<b>4.7</b>	Heat Effects of Industrial Reactions . . . . .	152
<b>4.8</b>	Synopsis . . . . .	163
<b>4.9</b>	Problems. . . . .	163
<b>5</b>	<b>THE SECOND LAW OF THERMODYNAMICS</b>	<b>173</b>
<b>5.1</b>	Axiomatic Statements of the Second Law . . . . .	173
<b>5.2</b>	Heat Engines and Heat Pumps . . . . .	178
<b>5.3</b>	Carnot Engine with Ideal-Gas-State Working Fluid . . . . .	179
<b>5.4</b>	Entropy . . . . .	180
<b>5.5</b>	Entropy Changes for the Ideal-Gas State . . . . .	182
<b>5.6</b>	Entropy Balance for Open Systems . . . . .	185
<b>5.7</b>	Calculation of Ideal Work . . . . .	190
<b>5.8</b>	Lost Work . . . . .	194
<b>5.9</b>	The Third Law of Thermodynamics . . . . .	197
<b>5.10</b>	Entropy from the Microscopic Viewpoint . . . . .	198
<b>5.11</b>	Synopsis . . . . .	200
<b>5.12</b>	Problems. . . . .	201
<b>6</b>	<b>THERMODYNAMIC PROPERTIES OF FLUIDS</b>	<b>210</b>
<b>6.1</b>	Fundamental Property Relations . . . . .	210
<b>6.2</b>	Residual Properties. . . . .	220
<b>6.3</b>	Residual Properties from the Virial Equations of State . . . . .	226
<b>6.4</b>	Generalized Property Correlations for Gases. . . . .	228
<b>6.5</b>	Two-Phase Systems . . . . .	235
<b>6.6</b>	Thermodynamic Diagrams . . . . .	243
<b>6.7</b>	Tables of Thermodynamic Properties . . . . .	245
<b>6.8</b>	Synopsis . . . . .	248
<b>6.9</b>	Addendum. Residual Properties in the Zero-Pressure Limit . . . . .	249
<b>6.10</b>	Problems. . . . .	250
<b>7.</b>	<b>APPLICATIONS OF THERMODYNAMICS TO FLOW PROCESSES</b>	<b>264</b>
<b>7.1</b>	Duct Flow of Compressible Fluids. . . . .	265
<b>7.2</b>	Turbines (Expanders) . . . . .	278

<b>7.3</b>	Compression Processes . . . . .	283
<b>7.4</b>	Synopsis . . . . .	289
<b>7.5</b>	Problems . . . . .	290
<b>8</b>	<b>PRODUCTION OF POWER FROM HEAT</b>	<b>299</b>
<b>8.1</b>	The Steam Power Plant. . . . .	300
<b>8.2</b>	Internal-Combustion Engines. . . . .	311
<b>8.3</b>	Jet Engines; Rocket Engines. . . . .	319
<b>8.4</b>	Synopsis . . . . .	321
<b>8.5</b>	Problems. . . . .	321
<b>9</b>	<b>REFRIGERATION AND LIQUEFACTION</b>	<b>327</b>
<b>9.1</b>	The Carnot Refrigerator . . . . .	327
<b>9.2</b>	The Vapor-Compression Cycle . . . . .	328
<b>9.3</b>	The Choice of Refrigerant . . . . .	331
<b>9.4</b>	Absorption Refrigeration . . . . .	334
<b>9.5</b>	The Heat Pump. . . . .	336
<b>9.6</b>	Liquefaction Processes . . . . .	337
<b>9.7</b>	Synopsis . . . . .	343
<b>9.8</b>	Problems. . . . .	343
<b>10</b>	<b>THE FRAMEWORK OF SOLUTION THERMODYNAMICS</b>	<b>348</b>
<b>10.1</b>	Fundamental Property Relation . . . . .	349
<b>10.2</b>	The Chemical Potential and Equilibrium . . . . .	351
<b>10.3</b>	Partial Properties . . . . .	352
<b>10.4</b>	The Ideal-Gas-State Mixture Model. . . . .	363
<b>10.5</b>	Fugacity and Fugacity Coefficient: Pure Species. . . . .	366
<b>10.6</b>	Fugacity and Fugacity Coefficient: Species in Solution . . . . .	372
<b>10.7</b>	Generalized Correlations for the Fugacity Coefficient . . . . .	379
<b>10.8</b>	The Ideal-Solution Model . . . . .	382
<b>10.9</b>	Excess Properties . . . . .	385
<b>10.10</b>	Synopsis . . . . .	389
<b>10.11</b>	Problems. . . . .	390
<b>11</b>	<b>MIXING PROCESSES</b>	<b>400</b>
<b>11.1</b>	Property Changes of Mixing . . . . .	400
<b>11.2</b>	Heat Effects of Mixing Processes. . . . .	405
<b>11.3</b>	Synopsis . . . . .	415
<b>11.4</b>	Problems. . . . .	415
<b>12</b>	<b>PHASE EQUILIBRIUM: INTRODUCTION</b>	<b>421</b>
<b>12.1</b>	The Nature of Equilibrium . . . . .	421
<b>12.2</b>	The Phase Rule. Duhem's Theorem. . . . .	422
<b>12.3</b>	Vapor/Liquid Equilibrium: Qualitative Behavior. . . . .	423
<b>12.4</b>	Equilibrium and Phase Stability. . . . .	435
<b>12.5</b>	Vapor/Liquid/Liquid Equilibrium . . . . .	439

<b>12.6</b>	Synopsis . . . . .	442
<b>12.7</b>	Problems . . . . .	443
<b>13</b>	<b>THERMODYNAMIC FORMULATIONS FOR VAPOR/ LIQUID EQUILIBRIUM</b>	<b>450</b>
<b>13.1</b>	Excess Gibbs Energy and Activity Coefficients . . . . .	451
<b>13.2</b>	The Gamma/Phi Formulation of VLE . . . . .	453
<b>13.3</b>	Simplifications: Raoult's Law, Modified Raoult's Law, and Henry's Law . . . . .	454
<b>13.4</b>	Correlations for Liquid-Phase Activity Coefficients . . . . .	468
<b>13.5</b>	Fitting Activity Coefficient Models to VLE Data . . . . .	473
<b>13.6</b>	Residual Properties by Cubic Equations of State . . . . .	487
<b>13.7</b>	VLE from Cubic Equations of State . . . . .	490
<b>13.8</b>	Flash Calculations . . . . .	503
<b>13.9</b>	Synopsis . . . . .	507
<b>13.10</b>	Problems . . . . .	508
<b>14</b>	<b>CHEMICAL-REACTION EQUILIBRIA</b>	<b>524</b>
<b>14.1</b>	The Reaction Coordinate . . . . .	525
<b>14.2</b>	Application of Equilibrium Criteria to Chemical Reactions . . . . .	529
<b>14.3</b>	The Standard Gibbs-Energy Change and the Equilibrium Constant . . . . .	530
<b>14.4</b>	Effect of Temperature on the Equilibrium Constant . . . . .	533
<b>14.5</b>	Evaluation of Equilibrium Constants . . . . .	536
<b>14.6</b>	Relation of Equilibrium Constants to Composition . . . . .	539
<b>14.7</b>	Equilibrium Conversions for Single Reactions . . . . .	543
<b>14.8</b>	Phase Rule and Duhem's Theorem for Reacting Systems . . . . .	555
<b>14.9</b>	Multireaction Equilibria . . . . .	559
<b>14.10</b>	Fuel Cells . . . . .	570
<b>14.11</b>	Synopsis . . . . .	574
<b>14.12</b>	Problems . . . . .	575
<b>15</b>	<b>TOPICS IN PHASE EQUILIBRIA</b>	<b>587</b>
<b>15.1</b>	Liquid/Liquid Equilibrium . . . . .	587
<b>15.2</b>	Vapor/Liquid/Liquid Equilibrium (VLLE) . . . . .	597
<b>15.3</b>	Solid/Liquid Equilibrium (SLE) . . . . .	602
<b>15.4</b>	Solid/Vapor Equilibrium (SVE) . . . . .	606
<b>15.5</b>	Equilibrium Adsorption of Gases on Solids . . . . .	609
<b>15.6</b>	Osmotic Equilibrium and Osmotic Pressure . . . . .	625
<b>15.7</b>	Synopsis . . . . .	629
<b>15.8</b>	Problems . . . . .	629
<b>16</b>	<b>THERMODYNAMIC ANALYSIS OF PROCESSES</b>	<b>636</b>
<b>16.1</b>	Thermodynamic Analysis of Steady-State Flow Processes . . . . .	636
<b>16.2</b>	Synopsis . . . . .	645
<b>16.3</b>	Problems . . . . .	645

<b>A Conversion Factors and Values of the Gas Constant</b>	<b>648</b>
<b>B Properties of Pure Species</b>	<b>650</b>
<b>C Heat Capacities and Property Changes of Formation</b>	<b>655</b>
<b>D The Lee/Kesler Generalized-Correlation Tables</b>	<b>663</b>
<b>E Steam Tables</b>	<b>680</b>
<b>F Thermodynamic Diagrams</b>	<b>725</b>
<b>G UNIFAC Method</b>	<b>730</b>
<b>H Newton's Method</b>	<b>737</b>
<b>Index</b>	<b>741</b>