Chemical and Process Thermodynamics

Third Edition

B. G. Kyle

Emeritus Professor of Chemical Engineering Kansas State University



Prentice Hall PTR Upper Saddle River, New Jersey 07458

CONTENTS

•

rı	erace		XIII
N	otation		xvii
1	Introduct	1	
	1-1	The Anatomy of Thermodynamics	1
	1-2	The Terminology of Thermodynamics	4
	1-3	The Variables and Quantities of Thermodynamics	5
	1-4	Equilibrium and the Equilibrium State	11
	1-5	The Phase Rule	12
	1-6	The Reversible Process	13
2	The First	Law of Thermodynamics	15
	2-1	The First Law and Internal Energy	15
	2-2	The Enthalpy	21
	2-3	The Heat Capacity	25
	2-4	The First Law for Open Systems	26
		Problems	35
3	The Beha	avior of Fluids	41
	3-1	The PVT Behavior of Fluids	42
	3-2	Equations of State	44
	3-3	The Ideal Gas	48
	3-4	The Compressibility Factor	55
	3-5	Generalized Equations of State	56
		Problems	64
4	The Seco	nd Law of Thermodynamics	69
	4-1	Heat Engines and the Carnot Cycle	70
	4-2	The Ideal-Gas Carnot Cycle	71

vii

...

Contents

197

4-3	The Absolute Temperature Scale	74
4-4	The Entropy Function	76
4-5	Entropy and the Spontaneity of Natural Processes	78
4-6	Calculation of Entropy Changes	79
4-7	Open Systems	87
4-8	Applications of the Second Law	88
4-9	The Microscopic View of Entropy	95
4-10	The Third Law of Thermodynamics	97
	Problems	98
The Ther	modynamic Network	103
5-1	The Free Energy Functions	104
5-2	The Clausius Inequality and the Fundamental Equation	104
5-3	The Thermodynamic Network	106
5-4	Measurable Quantities	108
5-5	Calculation of H and S as Functions of P and T	109
5-6	Property Estimation from Corresponding States	114
5-7	Property Estimation Via Generalized Equations of State	118
5-8*	The Method of Jacobians	124
5-9*	The Generality of the Thermodynamic Method	132
	Problems	138
Heat Effe	cts	149
6-1	The Computational Path	150
6-2	Heat Effects Due to Change of Temperature	151
6-3	Heat Effects Due to Change of Pressure	154
6-4	Heat Effects Due to Change of Phase	154

6-4	Heat Effects Due to Change of Phase	154
6-5	Mixing Heat Effecfts	155
6-6	Enthalpy-Concentration Diagrams	161
6-7	Chemical Heat Effects	166
6-8	Heats of Formation in Solution	173
6-9	Applied Thermochemistry	176
	Problems	189

7 Equilibrium and Stability

7-1 Criteria of Equilibrium 198 The Chemical Potential 7-2 200 Application of the Equilibrium Criteria 7-3 203 The Essence of Thermodynamics 7-4 206 7-5* Stability 208 7-6* Constraints, Equilibrium and Virtual Variations 214 Problems 215

viii

5

6

Co	Contents 8 Thermodynamics of Pure Substances 8-1 The Phase Diagram 8-2 The Clapeyron Equation 8-3 Solid-Liquid Equilibrium		
8	Thermody	vnamics of Pure Substances	217
	8-1	The Phase Diagram	217
	8-2	The Clapeyron Equation	220
	8-3	Solid-Liquid Equilibrium	223
	8-4	Solid-Vapor and Liquid-Vapor Equilibrium	225
	8-5	Presentation of Thermodynamic Property Data	229
		Problems	233
9	Principles	of Phase Equilibrium	239
	9-1	Presentation of Vapor-Liquid Equilibrium Data	240
	9-2	Determination of Vapor-Liquid Equilibrium Data	244
	9-3	The Thermodynamic Basis for the Phase Rule	246
	9-4	The Fugacity	247
	9-5	Determination of Fugacities of Pure Substances	249
	9-6	Determination of Fugacities in Mixtures	258
	9-7	Ideal Systems	261
	9-8	The Activity Coefficient	270
	9-9	Experimental Determination of Activity Coefficients	274
	9-10	Henry's Law	278
	9-11	Activity Coefficient Equations	279
	9-12	Phase Equilibrium Via an Equation of State	291
	9-13	The Thermodynamic Approach to Phase Equilibrium	299
		Problems	302
10	Applied 1	Phase Equilibrium	309
	10-1	The Consummate Thermodynamic Correlation	
		of Vapor-Liquid Equilibrium	313
	10-2	Constant-Pressure VLE Data	319
	10-3	Total Pressure Data	325
	10-4	Azeotropes	327
	10-5	Thermodynamic Consistency Tests	332
	10-6	Multicomponent Vapor-Liquid Equilibrium	337
	10-7	Phase Behavior in Partially Miscible Systems	340
	10-8	Liquid-Liquid Equilibrium	346
	10-9*	Ternary Liquid-Liquid Equilibrium	350
	10-10	Estimates from Fragmentary Data	352
	10-11	Recapitulation	359
		Problems	362

X			Contents		
11	Additional Topics in Phase Equilibrium				
	11-1	Partial Molar Properties	375		
	11-2	Experimental Determination of Mixture			
		and Partial Molar Properties	378		
	11-3	Mixture Properties for Ideal Solutions	384		
	11-4*	Activity Coefficients Based on Henry's Law	386		
	11-5*	The Solubility of Gases in Liquids	390		
	11-6*	Solid-Liquid Equilibria	394		
	11-7*	Solid-Supercritical Fluid Equilibrium	410		
	11-8*	Prediction of Solution Behavior	412		
		Problems	420		
12	Chemical	Equilibrium	433		
	12-1	Generalized Stoichiometry	435		
	12-2	The Condition of Equilibrium for a Chemical Reaction	437		
	12-3	Standard States and ΔG°	440		
	12-4	Temperature Dependence of the Equilibrium Constant	444		
	12-5	Experimental Determination of Thermochemical Data	446		
	12-6	Other Free Energy Functions	454		
	12-7	Homogeneous Gas-Phase Reactions	456		
	12-8	Heterogeneous Chemical Equilibrium	462		
	12-9	Reactions in Solution	468		
	12-10*	Reactions in Aqueous Solution	478		
		Electrolyte Solutions	486		
	12-12*	Coupled Reactions			
		Problems	511		
13	Complex	Chemical Equilibrium	435 437 440 444 446 454 456 462 468 478 486 505 511 529 530 548 557 571 579 581		
	13-1	The Phase Rule for Reacting Systems	530		
	13-2*	Analyzing Complex Chemical Equilibrium Problems	548		
	13-3*	Formulating Complex Chemical Equilibrium Problems	557		
	13-4*	The CHO System and Carbon Deposition Boundaries	571		
	13-5*	The Si-Cl-H System and Silicon Deposition Boundaries	579		
		Problems	581		
14	Thermody	ynamic Analysis of Processes	589		
	14-1	Work and Free Energy Functions	589		
	14-2	The Availability	591		
	14-3	Mixing and Separation Processes	600		

ş.

Contents

	1, ,+	TT		(07		
	14-4*		at Exchange	607		
	14-5		tems Involving Chemical Transformations	614		
		Pro	blems	632		
15	Physicom	lecha	anical Processes			
	15-1	Con	npression and Expansion of Gases	640		
	15-2	The	Joule-Thomson Expansion	643		
	15-3	Liqu	uefaction of Gases	645		
	15-4	Refi	rigeration	654		
	15-5	Hea	at Pumps	661		
	15-6	Рои	ver Generation	662		
	15-7	Cog	generation of Steam and Power	667		
		Pro	blems	671		
16	Compressible Fluid Flow					
	16-1	The	Basic Equations of Fluid Mechanics	678		
	16-2		ic Velocity	681		
	16-3	Isen	ntropic Flow	683		
	16-4		ntropic Flow Through Nozzles	685		
	16-5		nisentropic Flow	689		
			blems	693		
17	Thermod	ynan	nics and Models	697		
	17-1*	Star	ndard Models	698		
	17-2*	Ad	Hoc Models	703		
	17-3*	Eva	uluation of Models	719		
		722				
Ap	pendix A			729		
	Table A	-1	Critical Constants of Selected Substances	729		
	Figure		Equilibrium Constants for Selected Reactions	731		
Ap	pendix B			732		
	Table B-1		Molar Heat Capacities of Gases at Zero Pressure	732		

xi

Xİİ		Cor	tents
Apper	ndix C		734
	Table C-1	Thermodynamic Properties of Saturated Steam	734
	Table C-2	Thermodynamic Properties of Superheated Steam	737
Appen	ıdix D		742
	Table D-1	Enthalpies and Free Energies of Formation	742
	Table D-2	of Selected Organic Compounds Enthalpies and Free Energies of Formation	
		of Selected Inorganic Compounds	744
	Table D-3	Free Energies of Formation of Selected Ions in the Aqueous State	745
Арреп	ndix E		746
	Inventory of	the CD-ROM	746
Appen	ndix F		751
	Properties of	f Determinants	751
Index			753