

Contents

Authors XIII

Preface XV

List of Symbols XIX

1	Introduction	1
2	PvT Behavior of Pure Components	5
2.1	General Description	5
2.2	Caloric Properties	10
2.3	Ideal Gases	14
2.4	Real Fluids	16
2.4.1	Auxiliary Functions	16
2.4.2	Residual Functions	17
2.4.3	Fugacity and Fugacity Coefficient	19
2.4.4	Phase Equilibria	23
2.5	Equations of State	27
2.5.1	Virial Equation	27
2.5.2	High Precision Equations of State	32
2.5.3	Cubic Equations of State	40
2.5.4	Generalized Equations of State and Corresponding States Principle	45
2.5.5	Advanced Cubic Equations of State	52
	Additional Problems	58
	References	61
3	Correlation and Estimation of Pure Component Properties	65
3.1	Characteristic Physical Property Constants	65
3.1.1	Critical Data	66
3.1.2	Acentric Factor	71
3.1.3	Normal Boiling Point	72
3.1.4	Melting Point and Enthalpy of Fusion	74
3.1.5	Standard Enthalpy and Standard Gibbs Energy of Formation	77
3.2	Temperature-Dependent Properties	80

3.2.1	Vapor Pressure	82
3.2.2	Liquid Density	94
3.2.3	Enthalpy of Vaporization	97
3.2.4	Ideal Gas Heat Capacity	102
3.2.5	Liquid Heat Capacity	109
3.2.6	Speed of Sound	113
3.3	Correlation and Estimation of Transport Properties	114
3.3.1	Liquid Viscosity	114
3.3.2	Vapor Viscosity	120
3.3.3	Liquid Thermal Conductivity	125
3.3.4	Vapor Thermal Conductivity	130
3.3.5	Surface Tension	133
3.3.6	Diffusion Coefficients	136
	Additional Problems	141
	References	143
4	Properties of Mixtures	147
4.1	Property Changes of Mixing	148
4.2	Partial Molar Properties	149
4.3	Gibbs–Duhem Equation	153
4.4	Ideal Mixture of Ideal Gases	154
4.5	Ideal Mixture of Real Fluids	156
4.6	Excess Properties	157
4.7	Fugacity in Mixtures	159
4.7.1	Fugacity of an Ideal Mixture	159
4.7.2	Phase Equilibrium	160
4.8	Activity and Activity Coefficient	161
4.9	Application of Equations of State to Mixtures	162
4.9.1	Virial Equation	163
4.9.2	Cubic Equations of State	164
	Additional Problems	174
	References	175
5	Phase Equilibria in Fluid Systems	177
5.1	Thermodynamic Fundamentals	186
5.2	Application of Activity Coefficient Models	193
5.3	Calculation of Vapor–Liquid Equilibria Using g^E -Models	197
5.4	Fitting of g^E -Model Parameters	216
5.4.1	Check of VLE Data for Thermodynamic Consistency	221
5.4.2	Recommended g^E -Model Parameters	231
5.5	Calculation of Vapor–Liquid Equilibria Using Equations of State	235
5.5.1	Fitting of Binary Parameters of Cubic Equations of State	240
5.6	Conditions for the Occurrence of Azeotropic Behavior	248
5.7	Solubility of Gases in Liquids	259
5.7.1	Calculation of Gas Solubilities Using Henry Constants	261

5.7.2	Calculation of Gas Solubilities Using Equations of State	270
5.7.3	Prediction of Gas Solubilities	271
5.8	Liquid–Liquid Equilibria	273
5.8.1	Temperature Dependence of Ternary LLE	286
5.8.2	Pressure Dependence of LLE	288
5.9	Predictive Models	289
5.9.1	Regular Solution Theory	290
5.9.2	Group Contribution Methods	292
5.9.3	UNIFAC Method	293
5.9.3.1	Modified UNIFAC (Dortmund)	300
5.9.3.2	Weaknesses of the Group Contribution Methods UNIFAC and Modified UNIFAC	309
5.9.4	Predictive Soave–Redlich–Kwong (PSRK) Equation of State	312
5.9.5	VTPR Group Contribution Equation of State	317
	Additional Problems	326
	References	330
6	Caloric Properties	333
6.1	Caloric Equations of State	333
6.1.1	Internal Energy and Enthalpy	333
6.1.2	Entropy	336
6.1.3	Helmholtz Energy and Gibbs Energy	337
6.2	Enthalpy Description in Process Simulation Programs	339
6.2.1	Route A: Vapor as Starting Phase	340
6.2.2	Route B: Liquid as Starting Phase	344
6.2.3	Route C: Equation of State	346
6.3	Caloric Properties in Chemical Reactions	354
6.4	The G-Minimization Technique	361
	Additional Problems	364
	References	364
7	Electrolyte Solutions	365
7.1	Introduction	365
7.2	Thermodynamics of Electrolyte Solutions	369
7.3	Activity Coefficient Models for Electrolyte Solutions	374
7.3.1	Debye–Hückel Limiting Law	374
7.3.2	Bromley Extension	376
7.3.3	Pitzer Model	377
7.3.4	Electrolyte-NRTL Model by Chen	378
7.3.5	LIQUAC Model	387
7.3.6	MSA Model	396
7.4	Dissociation Equilibria	396
7.5	Influence of Salts on the Vapor-Liquid Equilibrium Behavior	398
7.6	Complex Electrolyte Systems	400

Additional Problems 401

References 402

8 Solid-Liquid Equilibria 405

8.1 Thermodynamic Relations for the Calculation of Solid-Liquid Equilibria 408

8.1.1 Solid-Liquid Equilibria of Simple Eutectic Systems 410

8.1.1.1 Freezing Point Depression 417

8.1.2 Solid-Liquid Equilibria of Systems with Solid Solutions 419

8.1.2.1 Ideal Systems 419

8.1.2.2 Solid-Liquid Equilibria for Nonideal Systems 420

8.1.3 Solid-Liquid Equilibria with Intermolecular Compound Formation in the Solid State 424

8.1.4 Pressure Dependence of Solid-Liquid Equilibria 427

8.2 Salt Solubility 427

8.3 Solubility of Solids in Supercritical Fluids 432

Additional Problems 434

References 437

9 Membrane Processes 439

9.1 Osmosis 439

9.2 Pervaporation 443

Additional Problems 444

References 444

10 Polymer Thermodynamics 445

10.1 Introduction 445

10.2 g^E -models 451

10.3 Equations of State 462

10.4 Influence of Polydispersity 479

Additional Problems 482

References 484

11 Applications of Thermodynamics in Separation Technology 487

11.1 Verification of Model Parameters Prior to Process Simulation 492

11.1.1 Verification of Pure Component Parameters 492

11.1.2 Verification of g^E -Model Parameters 493

11.2 Investigation of Azeotropic Points in Multicomponent Systems 501

11.3 Residue Curves, Distillation Boundaries, and Distillation Regions 503

11.4 Selection of Entrainers for Azeotropic and Extractive Distillation 511

11.5 Selection of Solvents for Other Separation Processes 518

11.6 Examination of the Applicability of Extractive Distillation for the Separation of Aliphatics from Aromatics 519

Additional Problems 522
References 523

12	Enthalpy of Reaction and Chemical Equilibria	525
12.1	Enthalpy of Reaction	526
12.1.1	Temperature Dependence	527
12.1.2	Consideration of the Real Gas Behavior on the Enthalpy of Reaction	529
12.2	Chemical Equilibrium	531
12.3	Multiple Chemical Reaction Equilibria	551
12.3.1	Relaxation Method	552
12.3.2	Gibbs Energy Minimization	556
	Additional Problems	563
	References	565

13	Special Applications	567
13.1	Formaldehyde Solutions	567
13.2	Vapor Phase Association	573
	Additional Problems	587
	References	589

14	Practical Applications	591
14.1	Flash	591
14.2	Joule–Thomson Effect	593
14.3	Adiabatic Compression and Expansion	595
14.4	Pressure Relief	600
14.5	Limitations of Equilibrium Thermodynamics	606
	Additional Problems	608
	References	610

15	Introduction to the Collection of Example Problems	613
15.1	Mathcad Examples	613
15.2	Examples Using the Dortmund Data Bank (DDB) and the Integrated Software Package DDBSP	615
15.3	Examples Using Microsoft Excel and Microsoft Office VBA	616

Appendix A Pure Component Parameters 619

Appendix B Coefficients for High Precision Equations of State 641

Appendix C Useful Derivations 645

A1.	Relationship between $(\partial s/\partial T)_P$ and $(\partial s/\partial T)_V$	646
A2.	Expressions for $(\partial u/\partial v)_T$ and $(\partial s/\partial v)_T$	646
A3.	c_P and c_V as Derivatives of the Specific Entropy	647
A4.	Relationship between c_P and c_V	648

- A5. Expression for $(\partial h/\partial P)_T$ 649
- A6. Expression for $(\partial s/\partial P)_T$ 650
- A7. Expression for $[\partial(g/RT)/\partial T]_P$ and van't Hoff Equation 651
- A8. General Expression for c_v 651
- A9. Expression for $(\partial P/\partial v)_T$ 652
- A10. Cardano's Formula 652
- B1. Derivation of the Kelvin Equation 653
- B2. Equivalence of Chemical Potential μ and Gibbs Energy g for a Pure Substance 654
- B3. Phase Equilibrium Condition for a Pure Substance 655
- B4. Relationship between Partial Molar Property and State Variable (Euler Theorem) 657
- B5. Chemical Potential in Mixtures 658
- B6. Relationship between Second Virial Coefficients of Leiden and Berlin Form 659
- B7. Derivation of Expressions for the Speed of Sound for Ideal and Real Gases 659
- B8. Activity of the Solvent in an Electrolyte Solution 661
- B9. Temperature Dependence of the Azeotropic Composition 662
- C1. $(s-s^{id})_{T,P}$ 664
- C2. $(h-h^{id})_{T,P}$ 665
- C3. $(g-g^{id})_{T,P}$ 665
- D1. Fugacity Coefficient for a Pressure-Explicit Equation of State 665
- D2. Fugacity Coefficient of the Virial Equation (Leiden Form) 666
- D3. Fugacity Coefficient of the Virial Equation (Berlin Form) 668
- D4. Fugacity Coefficient of the Soave-Redlich-Kwong Equation of State 669
- D5. Fugacity Coefficient of the PSRK Equation of State 671
- E1. Derivation of the Wilson Equation 675
- E2. Notation of the Wilson, NRTL, and UNIQUAC Equations in Process Simulation Programs 678
- E3. Inability of the Wilson Equation to Describe a Miscibility Gap 679
- F1. $(h-h^{id})$ for Soave-Redlich-Kwong Equation of State 681
- F2. $(s-s^{id})$ for Soave-Redlich-Kwong Equation of State 683
- F3. $(g-g^{id})$ for Soave-Redlich-Kwong Equation of State 683
- F4. Antiderivatives of c_p^{id} Correlations 683
- G1. Speed of Sound as Maximum Velocity in an Adiabatic Pipe with Constant Cross-Flow Area 685
- G2. Maximum Mass Flux of an Ideal Gas 685
- References 687

Appendix D Standard Thermodynamic Properties for Selected Electrolyte Compounds 689

Appendix E Regression Technique for Pure Component Data 691

Appendix F Regression Techniques for Binary Parameters 695

References 709

**Appendix G Ideal Gas Heat Capacity Polynomial Coefficients for Selected
Compounds** 711

Appendix H UNIFAC Parameters 713

Appendix I Modified UNIFAC Parameters 715

Appendix J PSRK Parameters 721

Appendix K VTPR Parameters 725

References 727

Index 729