Contents

| 1 | Summary of Basic Thermodynamic Concepts: A Refresher | |
|------------|---|----|
| 1.1 | Introduction | 1 |
| 1.2 | Gibbs Energy as a State Function | 2 |
| 1.2.1 | Temperature and Pressure Dependence of Gibbs | |
| | Energy, and the Choice of a Standard State | 2 |
| 1.2.2 | Composition Dependence of Gibbs Energy | 7 |
| 1.2.2.1 | Chemical Potential and the | |
| | Gibbs-Duhem Equation | 7 |
| 1.2.2.2 | Property Changes on Mixing | 14 |
| 1.2.2.3 | Activity, Activity Coefficient, and Standard State. | 16 |
| 1.2.2.4 | Ideal, Excess, and Total Molar Properties | 20 |
| 1.2.2.5 | Some Properties of Ideal Solutions | 22 |
| 1.2.2.6 | Excess Molar Properties of Mixing | 24 |
| 1.3 | Mineral Equilibria, Equilibrium Constant | 30 |
| 2 | Measurement, Evaluation, and Tabulation of Thermodynamic Properties | |
| 2.1 | Introduction | 33 |
| 2.2 | Outlines of Some Calorimetric Methods | 34 |
| 2.2.1 | Calorimetry of Non-Reacting Systems | 34 |
| 2.2.2 | Calorimetry of Reacting Systems | 39 |
| 2.3 | Outlines of Electrochemical Cell Measurements. | 42 |
| 2.4 | Evaluation and Tabulation | 43 |
| 2.5 | of Thermodynamic Data | 43 |
| 2.3 | | 49 |
| | of Data | 49 |
| 3 | Equations of State for Fluids and Fluid Mixtures | i |
| 3.1 3.2 | Introduction | 55 |
| 3.4 | Fugacity, Activity | 55 |



| VIII | Contents |
|------|----------|
| | |

| 3.3 | Utility of the Volume Equations of State 59 |
|---------|--|
| 3.4 | Volume Equations of State for Pure Fluids 60 |
| 3.4.1 | General Comments and Literature Overview 60 |
| 3.4.2 | Some Examples of Analytical Equations of State . 64 |
| 3.4.3 | A Modified Redlich-Kwong (MRK) |
| | Equation of State for H ₂ O |
| 3.4.4 | Calculation of Phase Relations and Thermodynamic |
| | Properties of H ₂ O from MRK |
| 3.4.4.1 | Calculation of the Saturation Curve of H ₂ O 73 |
| 3.4.4.2 | Calculation of Fugacity and Molar Gibbs Energy |
| | of H_2O |
| 3.5 | Modified Redlich-Kwong Equation of State for |
| | a Fluid Mixture |
| 3.5.1 | Theoretical Background 78 |
| 3.5.2 | A Modified Redlich-Kwong Equation for the |
| | H ₂ O-CO ₂ Mixture 80 |
| 3.6 | Concluding Remarks |
| | |
| | |
| 4 | Phase Relations Among End-Member Solids |
| 4.1 | Introduction |
| 4.2 | Introduction |
| 4.3 | Error Propagation Calculation |
| 4.3.1 | Basic Formalism |
| 4.3.2 | Covariance of the Tabulated |
| | Thermodynamic Data 91 |
| 4.4 | Worked Examples |
| 4.5 | Concluding Remarks |
| | 105 |
| | |
| 5 | Phase Relations Among End-Member Solids |
| | and a Pure Fluid |
| 5.1 | Town Lord |
| 5.2 | Introduction |
| 5.3 | Theoretical Background |
| 3.3 | Error Propagation Formalism for Solid-Fluid |
| 5.4 | Equilibria |
| 5.5 | Sample Calculations of Dehydration Equilibria 111 |
| 5.5 | Thermodynamic Interpolation and Extrapolation |
| | of Reaction Reversal Data, and Linear Summation |
| 5.5.1 | of Independent Equilibria |
| 5.5.2 | Theoretical Basis |
| 5.5.3 | Worked Examples of Dehydration Reactions |
| 2.2.3 | reactions 135 |
| | |

| 6 | Phase Relations Among End-Member Solids and a Binary Fluid Mixture | |
|----------------|--|------------|
| 6.1 | Introduction | 141 |
| 6.2 | Thermodynamic Background | 141 |
| 6.3 | Sample Calculation of Mixed-Volatile | |
| | (H_2O-CO_2) Equilibria | 145 |
| 6.4 | Interpolation, Extrapolation, and | |
| | Linear Summation of Reaction Reversal Data | |
| 6.5 | Concluding Remarks | 164 |
| 7 | Derivation of an Internally Consistent Thermodynamic Dataset by Mathematical Programming | |
| 7.1 | | 165 |
| 7.2 | | 166 |
| 7.3 | A Thermodynamic Model for Mathematical | |
| | | 169 |
| 7.4 | | 170 |
| 7.4.1 7.4.2 | | 170 |
| 7.4.2 7.5 | | 172 173 |
| 7.5.1 | Input Database | |
| 7.5.2 | Input Database | 174 |
| 7.5.2.1 | | 174 |
| 7.5.2.2 | | 176 |
| 7.5.2.3 | Application of Linear Programming | 179 |
| 7.5.2.4 | | 181 |
| 7.5.2.5 | Application of Quadratic Programming | 182 |
| 7.5.2.6 | An Internally Consistent Thermodynamic | |
| | Dataset for the Three Al ₂ SiO ₅ Phases | |
| | by Quadratic Programming | 184 |
| 7.6 | Future Perspectives and Concluding Remarks | 190 |
| 8 | Thermodynamics of Crystalline Solutions | |
| 8.1 | Introduction, Scope, Definitions | 193 |
| 8.2 | Extension of the Thermodynamic Theory of | |
| | Molecular Solutions to Crystalline Solutions | 194 |
| 8.2.1 | | 194 |
| 8.2.2 | Derivation of Equations for Simple Crystalline | |
| | | 195 |
| 8.2.2.1 | | 195 |
| 8.2.2.2 | Simple Crystalline Solutions with Charge-Coupled Site Mixing on Two Sublattices | 204 |
| | SHE MIXING ON TWO SUDIAITICES | 414 |

X Contents

| 8.2.3 | Thermodynamic Treatment of Complex Crystallin | 1e |
|---------|---|-------|
| 8.3 | Solutions | . 201 |
| 0.5 | Crystelline Solutions | 211 |
| 8.4 | Crystalline Solutions | 211 |
| 8.4.1 | Phase Relations in a Binary Solution | . 213 |
| | Isostructural Solution | . 213 |
| 8.4.2 | Non-isostructural Solution | 218 |
| 8.5 | Formulation of Equations of State for | |
| 0.5.4 | Crystalline Solutions | 219 |
| 8.5.1 | Introduction | . 219 |
| 8.5.2 | Manipulation of Molar Quantity vs | |
| | Composition Data | . 220 |
| 8.5.2.1 | General Formalisms | . 220 |
| 8.5.2.2 | An Example of Processing Calorimetric Data | . 223 |
| 8.5.2.3 | Examples of Fitting $V(X)$ Data for | |
| | Crystalline Solutions | 227 |
| 8.5.3 | Handling Experimental Data on the Composition | |
| | Dependence of Partial Molar Quantities of | |
| | Mixing of a Component | 230 |
| 8.5.3.1 | Formalisms of Gibbs-Duhem Integration | 230 |
| 8.5.3.2 | Worked Examples of Gibbs-Duhem Integration . | 232 |
| 8.5.3.3 | An Alternative to Gibbs-Duhem Integration | 237 |
| 8.5.4 | More on Equations of State for | . 231 |
| 0.5.1 | Crystalline Solutions: Some Worked Examples | 240 |
| 8.5.4.1 | An Equation of State for the Halite-Sylvite | . 240 |
| 0.5.7.1 | | 240 |
| 8.5.4.2 | Crystalline Solution, (Na,K)Cl | 240 |
| 0.3.4.2 | Excess Mixing Properties of the Monticellite- | |
| 0 5 4 2 | Forsterite Crystalline Solution, (Ca,Mg)MgSiO ₄ . | 244 |
| 8.5.4.3 | Thermodynamic Mixing Properties of | |
| 0 ~ 4 4 | Zn(Al,Cr) ₂ O ₄ Spinel | . 247 |
| 8.5.4.4 | Solution Modeling of Grossular-Almandine | |
| | Garnets | . 252 |
| 8.6. | An Epilogue | 256 |
| 9 | Phase Equilibria Involving Nonideal Solutions a Outlines of Geothermometry and Geobarometr | and |
| | · | • |
| 9.1 | Introduction and Scope | 257 |
| 9.2 | Calculation of Heterogeneous Phase Equilibria | |
| | Involving Nonideal Solutions | . 258 |
| 9.2.1 | General Considerations | 258 |
| 9.2.2 | A Qualitative Look at the | |
| | Gibbs Energy Minimization Method | 258 |
| 9.2.2.1 | Theoretical Basis | 258 |
| 9.2.2.2 | Graphical Analysis of Isobaric-Isothermal | -20 |
| | G-X Sections | 250 |
| | | |

| 9.2.2.3 | From Isobaric-Isothermal G-X Sections to | |
|--|---|------|
| | Phase Diagrams | 261 |
| 9.2.3 | Alternative Techniques for Phase Diagram | |
| | Calculations with Nonideal Solutions, and Some | |
| | Worked Examples | 262 |
| 9.2.3.1 | Calculation of P-T-X Phase Diagram for the | |
| | NaAlSi ₃ O ₈ -KAlSi ₃ O ₈ Binary | 263 |
| 9.2.3.1.1 | Calculation of the Isobaric $T-X_{kf}$ Section | |
| | for the NaAlSi ₃ O ₈ -KAlSi ₃ O ₈ Binary: | |
| | the Analbite-Sanidine Solvus | 263 |
| 9.2.3.1.2 | Calculation of the P- X_{kf} Section Through the | |
| | NaAlSi ₃ O ₈ -KAlSi ₃ O ₈ Pseudobinary, and the P-T | |
| | Diagram | 268 |
| 9.2.3.2 | $NaAl_2[AlSi_3O_{10}(OH)_2]-KAl_2[AlSi_3O_{10}(OH)_2]$ | |
| | Pseudobinary: Computation of Phase Relations | |
| | for Multiple Equilibria | 272 |
| 9.2.3.3 | Computation of a T- X_{CO2} Phase Diagram with | |
| | a Crystalline Solution | 276 |
| 9.3 | Outlines of Geothermometry and Geobarometry. | 279 |
| 9.3.1 | Scope | |
| 9.3.2 | Some Fundamental Considerations | 280 |
| 9.3.2.1 | Identification of Equilibrium Mineral | |
| ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | | 280 |
| 9.3.2.2 | Thermodynamic Basis for the Evaluation | |
|).J.Z.Z. | of the Intensive Variables | 281 |
| 9.3.2.3 | Choice of Equilibria Appropriate | |
| 7.3.2.3 | for Geothermometry and Geobarometry | 281 |
| 9.3.3 | Setting up Geobarometers and Geothermometers . | 282 |
| 9.3.3.1 | Calibration of Geobarometers | 284 |
| 9.3.3.2 | Calibration of Exchange Geothermometers | |
| 9.3.4 | Limits of Applicability and Evaluation | |
| 7.5.7 | of Uncertainties in Geothermometry and | |
| | Geobarometry | 294 |
| 9.3.4.1 | Limits of Applicability | 294 |
| 9.3.4.2 | Evaluation of Uncertainties | |
| 9.3.5 | Two Worked Examples of Geothermometry, | |
| 7.5.5 | Geobarometry, and Geohygrometry | 297 |
| 9.3.5.1 | Staurolite- and Sillimanite-Bearing Metapelitic | |
| 7.5.5.1 | Rocks, Rangeley Quadrangle, Maine | 297 |
| 9.3.5.2 | Staurolite-Kyanite-Bearing Metapelites | |
| 7.0.0.2 | from the Great Smoky Mountains, North Carolina | 301 |
| 9.3.6 | Concluding Remarks | 304 |
| 7.5.0 | Concluding Remarks | ./0- |
| Reference | PS | 305 |
| 1401010110 | | |
| Subject I | ndex , , | 319 |