### Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts

#### TABLE OF CONTENTS

Page

COPYRIGHT; ADDITIONAL COPIES FOREWORD PREFACE	
hapter 1	Robert C. Newto
THERMODYNAMIC ANA	ALYSIS OF PHASE EQUILIBRIA
IN SIMPLE I	MINERAL SYSTEMS
General approach Enstatite and forsterite Pyrope Spinel - a disordered phase MgTs - a fictive substance Cordierite in peridotites ALUMINUM SILICATES CALCIUM-ALUMINUM SILICATES	
napter 2	Alexandra Navrotsk
MODELS OF CR	YSTALLINE SOLUTIONS
THE IDEAL SOLUTION THE ENTRO REGULAR, SUBREGULAR AND GENE SYSTEMATICS IN MIXING PROPERT PHASES WITH DIFFERENT STRUCTU ORDER-DISORDER IN SOLID SOLUT General comments Cation interchange equilibria, e	DPY OF MIXING TERM ERALIZED MIXING MODELS TES TRES TONS Specially in spinels
	FOREWORD PREFACE  THERMODYNAMIC ANA IN SIMPLE IN  INTRODUCTION MgO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> PERIDOTITE MINI General approach Enstatite and forsterite Pyrope Spinel - a disordered phase MgTs - a fictive substance Cordierite in peridotites ALUMINUM SILICATES CALCIUM-ALUMINUM SILICATES CONTINUOUS DEHYDRATION REACE FERROUS IRON MINERALS SUMMARY ACKNOWLEDGMENTS REFERENCES  IMPEREDICAN INTRODUCTION SOME THERMODYNAMIC FORMALI THE IDEAL SOLUTION THE ENTRO REGULAR, SUBREGULAR AND GENE SYSTEMATICS IN MIXING PROPERT PHASES WITH DIFFERENT STRUCTU ORDER-DISORDER IN SOLID SOLUT General comments Cation interchange equilibria, e Carbonates - calcite and dolomi Feldspar solid solutions CONCLUSIONS ACKNOWLEDGMENTS

## THERMODYNAMICS OF MULTICOMPONENT SYSTEMS CONTAINING SEVERAL SOLID SOLUTIONS

71	COMPUTATION OF MULTICOMPONENT, MULTIPHASE EQUILIBRIA
78	METHOD OF APPROACH
78	TREATMENT OF SOLID SOLUTIONS
79	Partial molar entropy of mixing
79	Excess free energies of mixing
80	THE SYSTEMS AS, MAS, CAS AND NAS
80	Albite
80	CaAl <sub>2</sub> SiO <sub>6</sub> pyroxene and anorthite
81	MgAl <sub>2</sub> O <sub>4</sub> Spinel
81	CMAS SYSTEM
81	Pyroxenes
83	Garnets
84	FeO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> System
84	Fayalite
84	Ferrosilite
84	Almandine
84	Hercynite
85	COMPLEX SOLID SOLUTIONS
85	Olivine
85	Garnet
85	Plagioclase
85	Pyroxenes
88	CALCULATION OF COMPLEX PHASE DIAGRAMS
90	SUMMARY
92	Adirondack granulites
93	ACKNOWLEDGMENTS
93	REFERENCES

#### Chapter 4

Kenneth S. Pitzer

## A THERMODYNAMIC MODEL FOR AQUEOUS SOLUTIONS OF LIQUID-LIKE DENSITY

97	INTRODUCTION
98	NOTATION
00	EXCESS GIBBS ENERGY; ACTIVITY AND OSMOTIC COEFFICIENTS
100	Basic equation
03	Pure electrolytes
.05	Mixed electrolytes
.08	Neutral solutes
.09	Association equilibria
.11	TEMPERATURE AND PRESSURE EFFECTS ON STANDARD STATE PROPERTIES
.12	DATA BASE
.12	Standard-state values for 25°C
.12	Standard-state enthalpies, entropies, heat capacities, and volumes
16	Pure-electrolyte parameters for 25°C
.17	Pure-electrolyte parameters for high temperatures

121	MIXING PARAMETERS			
123 123				
123	Solubilities of solids			
123	Complex ion equilibria Vapor-phase equilibria			
125	Thermal properties			
125				
	SUPPLEMENTARY COMMENTS			
127	ACKNOWLEDGMENTS			
127	APPENDIX A: THEORETICAL BACKGROUND			
133				
	EXPRESSIONS			
138	REFERENCES			
Cl	hapter 5 John H. Wear			
	MODELS OF MINERAL SOLUBILITY IN CONCENTRATED			
	BRINES WITH APPLICATION TO FIELD OBSERVATIONS			
143	INTRODUCTION			
145	OVERVIEW OF THE MODEL			
148	MODELS FOR SYSTEMS SHOWING STRONG ASSOCIATION: ION PAIRS VS			
140	SPECIFIC INTERACTION			
153	INCLUSION OF TEMPERATURE AND PRESSURE AS VARIABLES			
155	MODELS FOR POORLY DETERMINED SYSTEMS			
155	COMPARISON OF HMW MODEL TO OTHER MODELS			
160	OVERVIEW OF THE APPLICATION OF MODELS TO NATURAL ENVIRONMENTS			
162	APPLICATION TO PERMIAN AND MIOCENE EVAPORITES IN THE SEAWATER SYSTEM			
166	APPLICATION TO RECENT AND PRESENT DAY EVAPORATION PROCESSES			
171	ACKNOWLEDGMENTS			
171	ACKNOWLEDGMENTS APPENDIX			
174	REFERENCES			
-, .				
C	chapter 6 Dimitri A. Sverjensky			
	CALCULATION OF THE THERMODYNAMIC PROPERTIES			
	OF AQUEOUS SPECIES AND THE SOLUBILITIES OF			
	MINERALS IN SUPERCRITICAL ELECTROLYTE SOLUTIONS			
177	INTRODUCTION			
177				
181	COMPUTATIONAL STRATEGY FOR MINERAL SOLUBILITY CALCULATIONS			
	COMPUTATIONAL STRATEGY FOR MINERAL SOLUBILITY CALCULATIONS HYDROLYSIS CONSTANTS FOR MINERALS			
181	HYDROLYSIS CONSTANTS FOR MINERALS			
181 182	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals			
181 182 182	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases			
182	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals			
182 182 186 188	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes			
182 182 186	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes Standard molal entropies, heat capacities and volumes of complexes at 25 °C			
182 182 186 188 188	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes Standard molal entropies, heat capacities and volumes of complexes at 25 °C and 1 bar			
182 182 186 188 188	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes Standard molal entropies, heat capacities and volumes of complexes at 25°C and 1 bar Equation of state coefficients for aqueous complexes			
182 182 186 188 188 191 195	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes Standard molal entropies, heat capacities and volumes of complexes at 25 °C and 1 bar Equation of state coefficients for aqueous complexes ACTIVITY COEFFICIENTS OF SOLUTE SPECIES AND ACTIVITY OF THE SOLVENT			
182 182 186 188 188 191 195 195	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes Standard molal entropies, heat capacities and volumes of complexes at 25 °C and 1 bar Equation of state coefficients for aqueous complexes  ACTIVITY COEFFICIENTS OF SOLUTE SPECIES AND ACTIVITY OF THE SOLVENT Solute species			
182 182 186 188 188 191 195	HYDROLYSIS CONSTANTS FOR MINERALS Standard molal Gibbs free energies of minerals Standard molal Gibbs free energies of gases Standard molal Gibbs free energies of aqueous species DISSOCIATION CONSTANTS OF AQUEOUS SPECIES Standard molal Gibbs free energies of aqueous complexes Standard molal entropies, heat capacities and volumes of complexes at 25 °C and 1 bar Equation of state coefficients for aqueous complexes ACTIVITY COEFFICIENTS OF SOLUTE SPECIES AND ACTIVITY OF THE SOLVENT			

196	Neutral species
196	Activity of the solvent
197	COMPUTATIONAL APPROACH
197	ILLUSTRATIVE EXAMPLES
197	Aqueous speciation of lead and chloride in supercritical chloride-bearing fluids
200	Temperature dependence
200	Pressure dependence
200	Dependence on pH
201	Dependence on HCl°
201	Solubility of galena in supercritical chloride-bearing solutions
203	CONCLUDING REMARKS
204	ACKNOWLEDGMENTS
204	REFERENCES

#### Chapter 7

John R. Holloway

#### **IGNEOUS FLUIDS**

211	INTRODUCTION
212	PROPERTIES OF MOLECULAR SPECIES IN FLUIDS
212	
	Size and shape
212	Attractive forces between molecules
213	Permanent dipole-permanent dipole forces
214	Dispersion forces
214	Higher order permanent moments
215	Potential energy relations
215	Relative importance of attractive forces
217	EQUATIONS OF STATE
217	Two-parameter equations
218	Corresponding states
219	Empirical equations
219	Treatment of mixtures
219	THE NATURE OF IGNEOUS FLUIDS
221	Properties of H <sub>2</sub> O
221	Dissolved solutes
221	Silica
223	Alkali chlorides
223	The nature of igneous fluids in the crust and upper mantle
223	EQUILIBRIA IN C-O-H SYSTEMS
223	Free energy relations
225	Methods of equilibrium calculation
225	Minimization of total free energy
225	Equilibrium constants and mass balance
226	Solution for the C-O-H system
229	Graphite undersaturated fluid calculations
229	Representation of results
229	ADDITION OF OTHER COMPONENTS
231	Cl, F, and N
231	Modeling fluid/melt systems
231	IGNEOUS FLUID CALCULATIONS IN THE FUTURE
232	ACKNOWLEDGMENTS
232	REFERENCES

#### George H. Brimhall and David A. Crer

#### ORE FLUIDS: MAGMATIC TO SUPERGENE

235	INTRODUCTION
	Part I: The Generation of Magmas and Ore Fluids
236	PRE-METALLOGENIC HISTORY OF MAGMAS
237	GENERATION OF MAGMAS AND PLUTONS AT SUBDUCTION ZONES
237	Oceanic zones
239	Continental zones
240	CLASSES OF ORE-FORMING PLUTONS
240	Magmatic source rocks
240	Utility of biotite mineral chemistry
242	Hornblende, biotite, and muscovite
242	Classification by redox state and biotite halogen composition
243	Classification of granitic plutons by intensive variables
243	Oxygen fugacity
244	HF/H <sub>2</sub> O fugacity
	• • •
244	Correlation of ores with plutonic classes
246	Physical implications of magmatic water
246	Energy release
246	Hydrothermal convection
247	Lifetimes of hydrothermal systems
247	SOURCES AND GENERAL COMPOSITIONS OF HYDROTHERMAL SOLUTIONS
247	Sources of water
249	Composition
249	COMPOSITION OF MAGMATIC WATER
249	Water solubility in silicate melts
250	Partitioning of ore components between magmas and exsolving water
250	Chloride and sulfur
250	Cations and metals
252	Magmatic to hydrothermal transition: the biotite sensor
252	Compositions of hydrothermal biotites
254	Early high temperature hydrothermal oxidation
254	Relative importance of magmatic and meteoric waters
	Part II: Physical Chemistry of Hydrothermal Ore Fluids
255	SOLVENT-SOLUTE CONTROLS ON ORE SOLUTIONS
255	The water molecule
255	Water structure, hydrogen bonding and polarity
257	Dielectric constant of water
257	Solvating power of water
257	Coulomb's law
257	Hydration
259	Solvation energies
259	Effects of temperature and pressure on the dielectric constant
259	Temperature
260	Pressure
261	Effects of temperature and pressure on ionization
261	Other effects of pressure and temperature on water-solute interactions
261	Molecular vibration
261	Ligand field stabilization
263	Pressure-induced electron spin-pairing
263	TRANSITION METAL COMPLEX IONS
264	Geologically important ligands

265	Chemical controls		
265	Hard-soft behavior		
265	Electonegativity, LFSE and ionic potential		
268	Why solubilities increase with temperature		
270	RECENT EXAMPLES AND APPLICATIONS		
270	Molecular structures of complex ions		
272	Stoichiometries		
272	Stability constants		
274	Ore zoning		
275	Metal-organic complexing		
275	Activity coefficients		
276 277	Major salts Three main non-ideal effects		
277	Minor components in concentrated solutions		
279	Mineral solubility calculations from thermodynamic data		
281	How accurate are calculated solubilities?		
281	Estimating chemical conditions in mineral deposits		
201	Part III: Formation of Primary and Secondary Ore Deposits		
202	•		
283	PRIMARY ORE DEPOSITION		
283	Initial acidity		
284	Sulfur		
284 285	pH and alteration reactions		
	pH buffer capacity		
286 287	Boiling Remaining deposition controls		
287	Temperature		
287	Dilution		
287	Oxygen fugacity		
289	Multi-stage mineralization and ore metal remobilization		
289	Ore metal remobilization versus introduction		
290	Relationships of wall rock alteration to mineralization		
290	Hypogene leaching		
292	Thermodynamic modeling of hypogene oxidation and sulfidation: effects of		
	magmatic volatiles on hydrothermal fluids and protores		
292	Destruction of wall rock buffer control: the role of biotite		
294	Feedback of chemical reaction and fluid flow: Fluid dominated threshold state		
200	and the importance of the advanced argillic alteration mineral assemblage		
296	Epithermal systems: Manifestations of deep porphyry mineralization?		
296	SECONDARY ORE DEPOSITION		
296	Atmosphere-dominated states		
297	Constitutive mass balance models and simplified chemical controls		
297 298	Residual enrichment		
302	Supergene enrichment Thermodynamic and fluid flow modeling of supergene enrichment		
306	Hypogene enrichment by ferrolysis		
308	Internal factors		
308	Weathering paths in physical properties		
308	Primary permeability		
308	Available sulfur		
310	External factors		
310	Geomorphic conditions		
310	Optimal conditions for secondary enrichment and preservation		
310	Steady state versus transient flow effects		
311	ACKNOWLEDGMENTS		
311	REFERENCES		

# THERMODYNAMIC MODELS OF MOLECULAR FLUIDS AT THE ELEVATED PRESSURES AND TEMPERATURES OF CRUSTAL METAMORPHISM

202	The property of the second of
323	INTRODUCTION
326	THERMODYNAMICS OF FLUIDS WITH VARIABLES V AND T
326	Internal energy
328	Entropy
329	Helmholtz free energy
329	Chemical potential
329	Fugacity and fugacity coefficient
330	EQUATIONS OF STATE
330	Virial equation
330	One-component fluids
331	Fluid mixtures
333	Redlich-Kwong equation
333	One-component fluids
33 <b>5</b>	Relationship between Redlich-Kwong and virial equations
335	Fluid mixtures
340	FUGACITIES FROM EQUATIONS OF STATE
340	Fugacities from virial equation of state
341	Fugacities from Redlich-Kwong equation of state
342	A note on the Lewis and Randall Rule
345	EQUATIONS OF STATE IN THE GEOCHEMICAL/PETROLOGICAL LITERATURE
345	Virial equations of state,
346	Redlich-Kwong equations of state
346	Holloway-Flowers version
346	Bottinga-Touret-Richet version
348	Halbach-Chatterjee version
348	Bowers-Helgeson version
348	Kerrick-Jacobs version
352	MINERAL-FLUID EQUILIBRIA AND EVALUATION OF EQUATIONS OF STATE
352	Basic equation for mineral-fluid equilibrium
353	Equilibria and the thermodynamic data base
353	Diagrams to evaluate equations of state
354	Dolomite-quartz-talc-calcite
354	Calcite-quartz-wollastonite
356	Muscovite-calcite-quartz-sanidine-anorthite
356	Zoisite-calcite-anorthite
356	Discussion
358	APPLICATIONS OF THE REDLICH-KWONG EQUATION TO TERNARY AND
	HIGHER-ORDER FLUID SOLUTIONS
358	The system C-O-H
360	The system C-O-H-S
362	The system C-O-H-S-N
363	ACKNOWLEDGMENTS
363	REFERENCES
202	NEPERENCES

#### Chapter 10

#### Hans P. Eugster and Lukas Baumgartner

## MINERAL SOLUBILITIES AND SPECIATION IN SUPERCRITICAL METAMORPHIC FLUIDS

367	INTRODUCTION
368	EQUATION of STATE FOR SOLUTES
369	WATER AS A SOLVENT
371	The solvent
371	Quartz
373	Corundum
375	K-spar and muscovite
376	Albite and paragonite
376	Brucite and portlandite
376	Magnetite  Dissociation Constants of Children Constants From Constants Date
377	DISSOCIATION CONSTANTS OF CHLORIDE COMPLEXES FROM CONDUCTIVITY DATA HCl
377 377	NaCl
37 <i>7</i> 377	KCl
379	CaCl <sub>2</sub>
379	MgCl <sub>2</sub>
379	FeCl <sub>2</sub>
381	MINERAL SOLUBILITIES IN SUPERCRITICAL H <sub>2</sub> O-HCl MIXTURES
381	Background
381	Experimental methods
383	METAL-CHLORIDE FREE ENERGIES AND SPECIATION
383	KC1
385	NaCl
385	${ m MgCl}_2$
387	CaCl <sub>2</sub>
387	FeCl <sub>2</sub>
389	MnCl <sub>2</sub> and NiCl <sub>2</sub>
389	H <sub>2</sub> O-CO <sub>2</sub> MIXTURES AS SOLVENTS
391	ACTIVITY COEFFICIENTS
391	SPECIATION CALCULATIONS
391	The methodology
394	Speciation in the system MgO-CaO-SiO <sub>2</sub> -H <sub>2</sub> O-HCl
397	SUMMARY AND CONCLUSIONS
398	ACKNOWLEDGMENTS
308	REFERENCES

#### Chapter 11

R. G. Berman and T. H. Brown

#### DEVELOPMENT OF MODELS FOR MULTICOMPONENT MELTS:

#### ANALYSIS OF SYNTHETIC SYSTEMS

405	INTRODUCTION
406	THEORETICAL CONSIDERATIONS
408	Speciation models

410 411 412 412 414 416 417 418 419 422 426 427 427 437 437	Stoichiometric solution models  EXPERIMENTAL CONSTRAINTS  Thermodynamic properties of melts  Glass-liquid relationships  Heat capacity of glasses  Heat capacity of liquids  Volumetric properties of liquids  Enthalpy and entropy of formation  Mixing properties of liquids  Thermodynamic properties of minerals  METHODOLOGY  Calibration of thermodynamic models  Testing of calibrations  APPLICATIONS  Speciation models  Stoichiometric models  CONCLUSIONS  ACKNOWLEDGMENTS  REFERENCES	and fusion
Chapter 12 Mark S. Ghiorso		
	MODELING MAGMATIC SYSTEMS: '	THERMODYNAMIC RELATIONS
443 443 445 448 451 452 454 459 460 460 461 462 463	INTRODUCTION General constraints on the formulation of Review of models that satisfy the therm CALIBRATION METHODS CALCULATING SOLID-LIQUID EQUILIBRIA Notation and mathematical statement of An algorithm for finding the minimum Modeling irreversible reactions GENERALIZED THERMODYNAMIC POTENTIL Legendre transformations Minimization of generalized thermodynts SUMMARY REFERENCES	odynamic requirements  the problem of G
Ch	hapter 13 Mark S. (	Ghiorso and Ian S.E. Carmichael
	MODELING MAGMATIC SYSTEMS:	PETROLOGIC APPLICATIONS
467 467 473 473 476 478 486 490 491 495 495 497	INTRODUCTION THERMODYNAMIC CLASSIFICATION OF IGN ACTIVITY OF SILICA AND DEPTH OF ORIGIN Silica activity and magmas Silica activity of basic magmas and a pe FRACTIONAL CRYSTALLIZATION OF OLIVIN ASSIMILATION OF PELITE INTO THOLEITIC ISOCHORIC CRYSTALLIZATION ISOBARIC VESICULATION SUMMARY APPENDIX REFERENCES	NOF MAFIC MAGMAS  trogenetic grid  E THOLEIITIC MAGMA