

Thermodynamics of Geothermal Fluids

CONTENTS

- | | | |
|---------|---|--------------------------|
| 1-4 | Thermodynamics of Geothermal Fluids | <i>Stefánsson et al.</i> |
| 5-33 | The Molecular-Scale Fundament of Geothermal Fluid Thermodynamics | <i>Driesner</i> |
| 35-79 | Thermodynamics of Aqueous Species at High Temperatures and Pressures: Equations of State and Transport Theory | <i>Dolejš</i> |
| 81-133 | Mineral Solubility and Aqueous Speciation Under Hydrothermal Conditions to 300 °C – The Carbonate System as an Example | <i>Bénézech et al.</i> |
| 135-164 | Thermodynamic Modeling of Fluid-Rock Interaction at Mid-Crustal to Upper-Mantle Conditions | <i>Manning</i> |
| 165-218 | Speciation and Transport of Metals and Metalloids in Geological Vapors | <i>Pokrovski et al.</i> |
| 219-263 | Solution Calorimetry Under Hydrothermal Conditions | <i>Tremaine, Arcis</i> |
| 265-309 | Structure and Thermodynamics of Subduction Zone Fluids From Spectroscopic Studies | <i>Sanchez-Valle</i> |
| 311-350 | Thermodynamics of Organic Transformations in Hydrothermal Fluids | <i>Shock et al.</i> |

Thermodynamics of Geothermal Fluids

76

Reviews in Mineralogy and Geochemistry

76

TABLE OF CONTENTS

1

Thermodynamics of Geothermal Fluids

*Andri Stefánsson, Thomas Driesner,
Pascale Bénézech*

INTRODUCTION TO THE VOLUME	1
REFERENCES	4

2

The Molecular-Scale Fundament of Geothermal Fluid Thermodynamics

Thomas Driesner

INTRODUCTION	5
BASIC RELATIONS BETWEEN THE MOLECULAR SCALE AND THE MACROSCOPIC THERMODYNAMIC PROPERTIES OF GEOFLUIDS	8
Simplified descriptions of molecular interactions	9
Basic concepts of statistical thermodynamics	10
Fluctuations and thermodynamic properties	12
Understanding fluid thermodynamics from pair correlation functions	13
Molecular simulation.....	15
GENERAL MOLECULAR-SCALE FEATURES OF AQUEOUS GEOFLUIDS	16
Hydration of ions.....	17
Ion pairing and clustering.....	18
Speciation	19
EFFECTS OF TEMPERATURE, PRESSURE/DENSITY, AND CONCENTRATION ON THE HYDRATION OF IONS IN SOLUTION.....	20
Temperature, pressure and concentration effects on the of hydration shell structure.....	22
FLUID THERMODYNAMICS ON THE MACROSCOPIC AND MOLECULAR SCALES IN THE CRITICAL AND SUPERCRITICAL REGIONS.....	24
An explanation of the divergence of derivative thermodynamic properties near the critical point.....	24
The molecular-scale picture behind near-critical divergence	25

POSSIBLE FUTURE ROUTES TOWARDS IMPROVED THERMODYNAMIC MODELS FOR GEOTHERMAL FLUIDS FROM AMBIENT TO SUPERCRITICAL CONDITIONS	28
REFERENCES	30

3

Thermodynamics of Aqueous Species at High Temperatures and Pressures: Equations of State and Transport Theory

David Dolejš

INTRODUCTION	35
CONCENTRATION SCALES AND CONVERSION RELATIONSHIPS	36
CONVENTIONS FOR THERMODYNAMIC PROPERTIES.....	39
BASIC THERMODYNAMIC MODELS FOR AQUEOUS EQUILIBRIA.....	42
Approximations to the Gibbs energy function	42
Predictions using the solvent density	43
Predictions using the electrostatic theory	45
EQUATIONS OF STATE FOR AQUEOUS SPECIES.....	46
Thermodynamics of hydration	46
Macroscopic thermodynamic models.....	53
Electrostatic models	54
Density models	59
APPLICATIONS OF AQUEOUS THERMODYNAMICS TO FLUID-ROCK INTERACTIONS	64
Transport theory and estimation of fluid fluxes.....	65
CONCLUDING REMARKS AND PERSPECTIVES	70
ACKNOWLEDGMENTS.....	72
REFERENCES	72

4

Mineral Solubility and Aqueous Speciation Hydrothermal Conditions to 300 °C – The Carbonate System as an Example

*Pascale Bénézech, Andri Stefánsson,
Quentin Gautier, Jacques Schott*

INTRODUCTION	81
COMMON TECHNIQUES FOR EXPERIMENTS AT HYDROTHERMAL CONDITIONS.....	85
Batch reactors	86
Electrode systems and high temperature pH measurements and titrations	89
<i>In situ</i> vibrational and electronic spectroscopy	96
SPECIATION AND THERMODYNAMIC STABILITIES IN CARBON-CONTAINING AQUEOUS SOLUTIONS	97

Aqueous speciation of CO ₂ -bearing solutions.....	97
Molecular structure of various aqueous carbon species	102
CARBONATE SOLUBILITY AND MINERALIZATION.....	105
Calcite.....	106
Magnesium-carbonates.....	109
Dolomite.....	120
Siderite.....	121
CONCLUSION.....	124
ACKNOWLEDGMENTS.....	124
REFERENCES	124

5 Thermodynamic Modeling of Fluid-Rock Interaction at Mid-Crustal to Upper-Mantle Conditions

Craig E. Manning

INTRODUCTION	135
CHEMICAL POTENTIALS OF AQUEOUS SPECIES IN HIGH- <i>PT</i> FLUIDS	136
Standard state chemical potentials of aqueous species.....	136
Activity models for aqueous species	139
COMPARISON OF EXPERIMENTAL AND CALCULATED MINERAL SOLUBILITY	142
APPLICATIONS.....	146
Activity-activity diagrams	146
Homogeneous equilibria.....	148
The pH dependence of mineral solubility	150
Buffering of pH by rock-forming minerals	152
Salinity and saline brines.....	154
“Excess” solubility and identification of additional solutes	156
Concluding remarks.....	159
ACKNOWLEDGMENTS.....	160
REFERENCES	160

6 Speciation and Transport of Metals and Metalloids in Geological Vapors

*Gleb S. Pokrovski, Anastassia Y. Borisova,
Andrey Y. Bychkov*

INTRODUCTION	165
SPECIATION, THERMODYNAMICS, AND PARTITIONING OF METALS AND METALLOIDS IN GEOLOGICAL VAPORS	167
Volcanic vapors.....	167
Hydrothermal-magmatic vapors	171
Vapor-brine-supercritical fluid-silicate melt partitioning in experimental and natural systems.....	186

ROLE OF THE VAPOR-LIKE FLUIDS IN METAL AND METALLOID TRANSPORT IN NATURAL SYSTEMS AND THE FORMATION OF ORE DEPOSITS	192
Low-temperature boiling geothermal systems	192
Magmatic-hydrothermal systems	197
MAJOR CONCLUSIONS	204
REMAINING GAPS AND NEAR-FUTURE CHALLENGES	205
Analytical challenges.....	205
Experimental challenges.....	206
Modeling challenges.....	207
ACKNOWLEDGMENTS.....	208
REFERENCES	208

7

Solution Calorimetry Under Hydrothermal Conditions

Peter Tremaine, Hugues Arcis

INTRODUCTION	219
THERMODYNAMIC RELATIONS	220
Equations for the temperature and pressure dependence of Gibbs energies and equilibrium constants.....	220
Solvation effects	221
The temperature dependence of standard partial molar properties	224
“EQUATIONS OF STATE” FOR STANDARD PARTIAL MOLAR PROPERTIES	225
The “density” model.....	225
The Helgeson-Kirkham-Flowers-Tanger model.....	226
THERMODYNAMICS OF SOLUTION CALORIMETRY	228
Standard partial molar heat capacities and volumes.....	228
Standard partial molar enthalpies and heats of mixing	229
Excess properties	230
DENSIMETRY	233
Vibrating-tube densimeters.....	233
HEAT-CAPACITY CALORIMETRY	235
Pioneering studies.....	235
The Picker flow microcalorimeter	236
Twin-cell differential scanning nanocalorimeters and Calvet calorimeters	240
Integral heat of solution measurements	243
HEAT OF MIXING CALORIMETRY	245
Pioneering instruments	245
Power-compensated isothermal flow heat of mixing calorimeters.....	247
Flow heat of mixing cells in Calvet calorimeters	249
Steam-gas mixtures	252
Calibration of isothermal heat-of-mixing calorimeters	253
DISCUSSION	255
Current state-of-the-art for hydrothermal solution calorimetry.....	255
Data compilations	255
Some current areas for investigation	255

CONCLUDING REMARKS.....	257
ACKNOWLEDGMENTS.....	257
REFERENCES	257

8 Structure and Thermodynamics of Subduction Zone Fluids from Spectroscopic Studies

Carmen Sanchez-Valle

INTRODUCTION	265
CHEMISTRY AND STRUCTURE OF SUBDUCTION ZONE FLUIDS	266
Chemistry of subduction zone fluids	266
Polymerization of silicate components in high-pressure fluids.....	267
CONTROLS ON TRACE ELEMENT SPECIATION IN SUBDUCTION	
ZONE FLUIDS	272
STUDIES ON TRACE ELEMENT SPECIATION IN SUBDUCTION ZONE	
FLUIDS BY X-RAY ABSORPTION SPECTROSCOPY.....	273
X-ray absorption spectroscopy (XAS)	274
XAS measurements in high-pressure fluids	274
SPECIATION OF TRACE ELEMENTS IN SUBDUCTION ZONE FLUIDS	277
Speciation of High Field Strength Elements (HFSE).....	277
Speciation of Rare Earth Elements (REE)	281
MOBILIZATION AND FRACTIONATION OF TRACE ELEMENTS IN	
SUBDUCTION ZONES	284
High Field Strength Elements (HFSE)	284
Mobilization of REE and LREE/HREE fractionation	285
PRESSURE-VOLUME-TEMPERATURE-COMPOSITION (<i>PVT_x</i>) RELATIONS	
AND THERMODYNAMIC PROPERTIES OF AQUEOUS FLUIDS.....	285
Equations of state (EoS) for aqueous fluids	285
Experimental studies of <i>PVT_x</i> properties in aqueous systems	286
EQUATIONS OF STATE OF FLUIDS FROM SOUND VELOCITY	
MEASUREMENTS BY BRILLOUIN SPECTROSCOPY	287
Principles of Brillouin scattering spectroscopy	288
Brillouin spectroscopy of fluids under pressure	290
Determination of density from measured sound velocities	291
PHYSICO-CHEMISTRY OF AQUEOUS FLUIDS AT ELEVATED	
PRESSURES (> 0.5 GPa).....	292
Volumetric properties of high-pressure aqueous fluids (> 0.5 GPa).....	292
Solute-solvent interactions in salt solutions under pressure.....	295
Fugacity and activity of water in high-pressure salt solutions	297
CONCLUDING REMARKS AND OUTLOOK	301
ACKNOWLEDGMENTS.....	302
REFERENCES	302

9

Thermodynamics of Organic Transformations in Hydrothermal Fluids

*Everett L. Shock, Peter Canovas, Ziming Yang,
Grayson Boyer, Kristin Johnson, Kirtland Robinson,
Kristopher Fecteau, Todd Windman, Alysia Cox*

MESSAGES FROM NATURE	311
ORGANIC INVENTORY OF HYDROTHERMAL FLUIDS	311
HYDROTHERMAL ORGANIC TRANSFORMATION PROCESSES	315
THERMODYNAMIC EXPLANATIONS	320
Hydrocarbon dissolution	320
Hydration/dehydration.....	323
Oxidation/reduction.....	324
Relative stabilities.....	328
EXPERIMENTAL TESTS.....	332
Hydration/dehydration reactions	332
Oxidation/reduction reactions	335
Relative stabilities and irreversible reactions	337
FUTURE DIRECTIONS FOR HYDROTHERMAL ORGANIC TRANSFORMATIONS	341
REFERENCES	342