

Jibamitra Ganguly

Thermodynamics in Earth and Planetary Sciences

 Springer

Contents

1	Introduction	1
1.1	Nature and Scope of Thermodynamics	1
1.2	Irreversible and Reversible Processes	3
1.3	Thermodynamic Systems, Walls and Variables	4
1.4	Work	5
1.5	Stable and Metastable Equilibrium	9
1.6	Lattice Vibrations	10
1.7	Electronic Configurations and Effects of Crystal Fields	13
	1.7.1 Electronic Shells, Subshells and Orbitals	13
	1.7.2 Crystal or Ligand Field Effects	15
1.8	Some Useful Physical Quantities and Units	17
2	First and Second Laws	19
2.1	The First Law	20
2.2	Second Law: The Classic Statements	22
2.3	Carnot Cycle: Entropy and Absolute Temperature Scale	23
2.4	Entropy: Direction of Natural Processes and Equilibrium	27
2.5	Microscopic Interpretation of Entropy: Boltzmann Relation	29
	2.5.1 Summary of the Important Relations in the First and Second Laws	33
2.6	Entropy and Disorder: Mineralogical Applications	33
	2.6.1 Configurational Entropy	33
	2.6.2 Vibrational Entropy	38
	2.6.3 Configurational vs. Vibrational Entropy	40
2.7	First and Second Laws: Combined Statement	43
2.8	Condition of Thermal Equilibrium: An Illustrative Application of the Second Law	44
2.9	Limiting Efficiency of a Heat Engine and Heat Pump	46
	2.9.1 Heat Engine	46
	2.9.2 Heat Pump	47
	2.9.3 Heat Engines in Nature	49

3	Thermodynamic Potentials and Derivative Properties	53
3.1	Thermodynamic Potentials	53
3.2	Equilibrium Conditions for Closed Systems: Formulations in Terms of the Potentials	56
3.3	What is Free in Free Energy?	58
3.4	Maxwell Relations	58
3.5	Thermodynamic Square: A Mnemonic Tool	59
3.6	Vapor Pressure and Fugacity	61
3.7	Derivative Properties	63
3.7.1	Thermal Expansion and Compressibility	63
3.7.2	Heat Capacities	65
3.8	Grüneisen Parameter	68
3.9	P-T Dependencies of Coefficient of Thermal Expansion and Compressibility	71
3.10	Summary of Thermodynamic Derivatives	71
4	Third Law and Thermochemistry	73
4.1	The Third Law and Entropy	73
4.1.1	Observational Basis and Statement	73
4.1.2	Third Law Entropy and Residual Entropy	75
4.2	Behavior of the Heat Capacity Functions	76
4.3	Non-Lattice Contributions to Heat Capacity and Entropy of End-member Solids	80
4.3.1	Electronic Transitions	80
4.3.2	Magnetic Transitions	82
4.4	Unattainability of Absolute Zero	84
4.5	Thermochemistry: Formalisms and Conventions	85
4.5.1	Enthalpy of Formation	85
4.5.2	Hess' Law	87
4.5.3	Gibbs Free Energy of Formation	87
4.5.4	Thermochemical Data	88
5	Critical Phenomenon and Equations of States	91
5.1	Critical End Point	91
5.2	Near- and Super-Critical Properties	95
5.2.1	Divergence of Thermal and Thermo-Physical Properties	95
5.2.2	Critical Fluctuations	96
5.2.3	Super- and Near-Critical Fluids	98
5.3	Near-Critical Properties of Water and Magma-Hydrothermal Systems	99
5.4	Equations of State	102
5.4.1	Gas	103
5.4.2	Solid and Melt	111

6	Phase Transitions, Melting and Reactions of Stoichiometric Phases ..	115
6.1	Gibbs Phase Rule: Preliminaries	115
6.2	Phase Transformations and Polymorphism	116
6.2.1	Thermodynamic Classification of Phase Transformations	117
6.3	Landau Theory of Phase Transition	119
6.3.1	General Outline	119
6.3.2	Derivation of Constraints on the Second Order Coefficient	123
6.3.3	Effect of Odd Order Coefficient on Phase Transition ...	124
6.3.4	Order Parameter vs. Temperature: Second Order and Tricritical Transformations	124
6.3.5	Landau Potential vs. Order Parameter: Implications for Kinetics	126
6.3.6	Illustrative Application to a Mineralogical Problem ...	127
6.4	Reactions in the P-T Space	129
6.4.1	Conditions of Stability and Equilibrium	129
6.4.2	P-T Slope: Clayperon-Classius Relation	130
6.5	Temperature Maximum on Dehydration and Melting Curves	131
6.6	Extrapolation of Melting Temperature to High Pressures	135
6.6.1	Kraut-Kennedy Relation	136
6.6.2	Lindemann-Gilvarry Relation	138
6.7	Calculation of Equilibrium P-T Conditions of a Reaction	138
6.7.1	Equilibrium Pressure at a Fixed Temperature	138
6.7.2	Effect of Polymorphic Transition	143
6.8	Evaluation of Gibbs Energy and Fugacity at High Pressure Using Equations of States	145
6.8.1	Birch-Murnaghan Equation of State	146
6.8.2	Vinet Equation of State	146
6.8.3	Redlich-Kwong and Related Equations of State for Fluids	147
6.9	Schreinemakers' Principles	148
6.9.1	Enumerating Different Types of Equilibria	149
6.9.2	Self-consistent Stability Criteria	150
6.9.3	Effect of an Excess Phase	151
6.9.4	Concluding Remarks	151
7	Thermal Pressure, Earth's Interior and Adiabatic Processes	153
7.1	Thermal Pressure	153
7.1.1	Thermodynamic Relations	153
7.1.2	Core of the Earth	155
7.1.3	Magma-Hydrothermal System	157
7.2	Adiabatic Temperature Gradient	159
7.3	Temperature Gradients in the Earth's Mantle and Outer Core	161
7.3.1	Upper Mantle	161

7.3.2	Lower Mantle and Core	163
7.4	Isentropic Melting in the Earth's Interior	165
7.5	The Earth's Mantle and Core: Linking Thermodynamics and Seismic Velocities	169
7.5.1	Relations among Elastic Properties and Sound Velocities	169
7.5.2	Radial Density Variation	171
7.5.3	Transition Zone in the Earth's Mantle	175
7.6	Joule-Thompson Experiment of Adiabatic Flow	177
7.7	Adiabatic Flow with Change of Kinetic and Potential Energies	180
7.7.1	Horizontal Flow with Change of Kinetic Energy: Bernoulli Equation	181
7.7.2	Vertical Flow	182
7.8	Ascent of Material within the Earth's Interior	184
7.8.1	Irreversible Decompression and Melting of Mantle Rocks	185
7.8.2	Thermal Effect of Volatile Ascent: Coupling Fluid Dynamics and Thermodynamics	187
8	Thermodynamics of Solutions	189
8.1	Chemical Potential and Chemical Equilibrium	189
8.2	Partial Molar Properties	193
8.3	Determination of Partial Molar Properties	195
8.3.1	Binary Solutions	195
8.3.2	Multicomponent Solutions	197
8.4	Fugacity and Activity of a Component in Solution	200
8.5	Determination of Activity of a Component using Gibbs-Duhem Relation	203
8.6	Molar Properties of a Solution	205
8.6.1	Formulations	205
8.6.2	Entropy of Mixing and Choice of Activity Expression	207
8.7	Ideal Solution and Excess Thermodynamic Properties	207
8.7.1	Thermodynamic Relations	207
8.7.2	Ideality of Mixing: Remark on the Choice of Components and Properties	209
8.8	Solute and Solvent Behaviors in Dilute Solution	210
8.8.1	Henry's Law	210
8.8.2	Raoult's Law	213
8.9	Speciation of Water in Silicate Melt	215
8.10	Standard States: Recapitulations and Comments	219
8.11	Stability of a Solution	221
8.11.1	Intrinsic Stability and Instability of a Solution	221
8.11.2	Extrinsic Instability: Decomposition of a Solid Solution	225
8.12	Spinodal, Critical and Binodal (Solvus) Conditions	226
8.12.1	Thermodynamic Formulations	226

	8.12.2	Upper and Lower Critical Temperatures	232
8.13		Effect of Coherency Strain on Exsolution	234
8.14		Spinodal Decomposition	236
8.15		Solvus Thermometry	237
8.16		Chemical Potential in a Field	239
	8.16.1	Formulations	239
	8.16.2	Applications	240
8.17		Osmotic Equilibrium	244
	8.17.1	Osmotic Pressure and Reverse Osmosis	244
	8.17.2	Osmotic Coefficient	245
	8.17.3	Determination of Molecular Weight of a Solute	246
9		Thermodynamic Solution and Mixing Models: Non-electrolytes	249
9.1		Ionic Solutions	249
	9.1.1	Single Site, Sublattice and Reciprocal Solution Models	250
	9.1.2	Disordered Solutions	254
	9.1.3	Coupled Substitutions	255
	9.1.4	Ionic Melt: Temkin and Other Models	256
9.2		Mixing Models in Binary Systems	256
	9.2.1	Guggenheim or Redlich-Kister, Simple Mixture and Regular Solution Models	257
	9.2.2	Subregular Model	259
	9.2.3	Darken's Quadratic Formulation	261
	9.2.4	Quasi-Chemical and Related Models	263
	9.2.5	Athermal, Flory-Huggins and NRTL (Non-random Two Site) Models	266
	9.2.6	Van Laar Model	268
	9.2.7	Associated Solutions	270
9.3		Multicomponent Solutions	273
	9.3.1	Power Series Multicomponent Models	274
	9.3.2	Projected Multicomponent Models	275
	9.3.3	Comparison Between Power Series and Projected Methods	277
	9.3.4	Estimation of Higher Order Interaction Terms	277
	9.3.5	Solid Solutions with Multi-Site Mixing	278
	9.3.6	Concluding Remarks	278
10		Equilibria Involving Solutions and Gaseous Mixtures	281
10.1		Extent and Equilibrium Condition of a Reaction	281
10.2		Gibbs Free Energy Change and Affinity of a Reaction	283
10.3		Gibbs Phase Rule and Duhem's Theorem	284
	10.3.1	Phase Rule	285
	10.3.2	Duhem's Theorem	287
10.4		Equilibrium Constant of a Chemical Reaction	289
	10.4.1	Definition and Relation with Activity Product	289

	10.4.2	Pressure and Temperature Dependences of Equilibrium Constant	291
10.5		Solid-Gas Reactions	292
	10.5.1	Condensation of Solar Nebula	292
	10.5.2	Surface-Atmosphere Interaction in Venus	296
	10.5.3	Metal-Silicate Reaction in Meteorite Mediated by Dry Gas Phase	297
	10.5.4	Effect of Vapor Composition on Equilibrium Temperature: T vs. X_v Sections	299
	10.5.5	Volatile Compositions: Metamorphic and Magmatic Systems	303
10.6		Equilibrium Temperature Between Solid and Melt	305
	10.6.1	Eutectic and Peritectic Systems	305
	10.6.2	Systems Involving Solid Solution	308
10.7		Azeotropic Systems	310
10.8		Reading Solid-Liquid Phase Diagrams	312
	10.8.1	Eutectic and Peritectic Systems	312
	10.8.2	Crystallization and Melting of a Binary Solid Solution	314
	10.8.3	Intersection of Melting Loop and a Solvus	315
	10.8.4	Ternary Systems	317
10.9		Natural Systems: Granites and Lunar Basalts	319
	10.9.1	Granites	319
	10.9.2	Lunar Basalts	321
10.10		Pressure Dependence of Eutectic Temperature and Composition	322
10.11		Reactions in Impure Systems	324
	10.11.1	Reactions Involving Solid Solutions	324
	10.11.2	Solved Problem	329
	10.11.3	Reactions Involving Solid Solutions and Gaseous Mixture	331
10.12		Retrieval of Activity Coefficient from Phase Equilibria	335
10.13		Equilibrium Abundance and Compositions of Phases	337
	10.13.1	Closed System at Constant P-T	337
	10.13.2	Conditions Other than Constant P-T	342
11		Element Fractionation in Geological Systems	347
	11.1	Fractionation of Major Elements	347
		11.1.1 Exchange Equilibrium and Distribution Coefficient	347
		11.1.2 Temperature and Pressure Dependence of K_D	349
		11.1.3 Compositional Dependence of K_D	350
		11.1.4 Thermometric Formulation	353
	11.2	Trace Element Fractionation Between Mineral and Melt	354
		11.2.1 Thermodynamic Formulations	354
		11.2.2 Illustrative Applications	359
		11.2.3 Estimation of Partition Coefficient	360

11.3	Metal-Silicate Fractionation: Magma Ocean and Core Formation .	363
11.3.1	Pressure Dependence of Metal-Silicate Partition Coefficients	367
11.3.2	Pressure Dependence of Metal-Silicate Distribution Coefficients	369
11.3.3	Pressure Dependencies of Ni vs. Co Partition- and Distribution-Coefficients	370
11.4	Effect of Temperature and $f(\text{O}_2)$ on Metal-Silicate Partition Coefficient	372
12	Electrolyte Solutions and Electrochemistry	375
12.1	Chemical Potential	376
12.2	Activity and Activity Coefficients: Mean Ion Formulations	377
12.3	Mass Balance Relation	378
12.4	Standard State Convention and Properties	378
12.4.1	Solute Standard State	378
12.4.2	Standard State Properties of Ions	380
12.5	Equilibrium Constant, Solubility Product & Ion Activity Product	381
12.6	Ion Activity Coefficients and Ionic Strength	382
12.6.1	Debye-Hückel and Related Methods	382
12.6.2	Mean-Salt Method	384
12.7	Multicomponent High Ionic Strength and High P-T Systems	385
12.8	Activity Diagrams of Mineral Stabilities	389
12.8.1	Method of Calculation	389
12.8.2	Illustrative Applications	392
12.9	Electrochemical Cells and Nernst Equation	396
12.9.1	Electrochemical Cell and Half-cells	396
12.9.2	Emf of a Cell and Nernst Equation	397
12.9.3	Standard Emf of Half-Cell and Full-Cell Reactions	398
12.10	Hydrogen Ion Activity in Aqueous Solution: pH and Acidity	399
12.11	Eh-pH Stability Diagrams	399
12.12	Chemical Model of Sea Water	403
13	Surface Effects	409
13.1	Surface Tension and Energetic Consequences	409
13.2	Surface Thermodynamic Functions and Adsorption	411
13.3	Temperature, Pressure and Compositional Effects on Surface Tension	414
13.4	Crack Propagation	415
13.5	Equilibrium Shape of Crystals	416
13.6	Contact and Dihedral Angles	418
13.7	Dihedral Angle and Interconnected Melt or Fluid Channels	423
13.7.1	Connectivity of Melt Phase and Thin Melt Film in Rocks	423

13.7.2	Core Formation in Earth and Mars	425
13.8	Surface Tension and Grain Coarsening	428
13.9	Effect of Particle Size on Solubility	430
13.10	Coarsening of Exsolution Lamellae	432
13.11	Nucleation	434
13.11.1	Theory	434
13.11.2	Microstructures of Metals in Meteorites	436
13.12	Effect of Particle Size on Mineral Stability	438
Appendix A	Rate of Entropy Production and Kinetic Implications	443
A.1	Rate of Entropy Production: Conjugate Flux and Force in Irreversible Processes	443
A.2	Relationship Between Flux and Force	447
A.3	Heat and Chemical Diffusion Processes: Comparison with the Empirical Laws	448
A.4	Onsager Reciprocity Relation and Thermodynamic Applications	450
Appendix B	Review of Some Mathematical Relations	453
B.1	Total and Partial Differentials	453
B.2	State Function, Exact and Inexact Differentials, and Line Integrals	454
B.3	Reciprocity Relation	456
B.4	Implicit Function	457
B.5	Integrating Factor	458
B.6	Taylor Series	459
Appendix C	Estimation of Thermodynamic Properties of Solids	461
C.1	Estimation of C_p and S° of End-Members from Constituent Oxides	461
C.1.1	Linear Combination of Components	461
C.1.2	Volume Effect on Entropy	462
C.1.3	Electronic Ordering Effect on Entropy	462
C.2	Polyhedral Approximation: Enthalpy, Entropy and Volume	463
C.3	Estimation of Enthalpy of Mixing	466
C.3.1	Elastic Effect	466
C.3.2	Crystal-Field Effect	468
References		471
Author Index		491
Subject Index		497