

Ladislav Cemič

Thermodynamics in Mineral Sciences

An Introduction

With 82 Figures and 23 Tables

 Springer

Contents

Chapter 1 Definition of thermodynamic terms	1
1.1 Systems	1
1.2 Phase	2
1.3 Components	3
1.4 Functions and variables of state	5
1.5 The concept of thermodynamic equilibrium	7
1.6 Temperature	7
1.7 Pressure	10
1.8 Composition	10
1.8. 1. Graphic representation of composition	11
1.9 Problems	21
 Chapter 2 Volume as a state function	23
2.1 Volume of pure phases	23
2.1.1 Thermal expansion and compressibility	25
Examples of calculated thermal expansion and compressibility	28
2.1.2 Volume of ideal gases as a state function	34
2.1.3 Volume of real gases	37
2.1.4 Volume of solid phases	43
Calculation of molar volume using x-ray diffraction data	46
2.2 Volume of solutions	47
2.2.1 Partial molar volume	48
2.2.2 Volume relationships in binary solutions	51
2.2.3 Volume changes on mixing	56
2.2.4 Examples for the volumes of binary solutions	60
2.2.5 Volume of reaction	73
2.3 Problems	75
 Chapter 3 The first law of thermodynamics	78
3.1 The relationship between heat and work	78
3.2 Internal Energy	78
3.2.1 Work	79
3.2.2 Enthalpy	83
3.3 Application of the first law of thermodynamics to pure phases	84

3.3.1 Heat capacities C_v and C_p	86
The temperature dependence of heat capacity	91
The empirical representation of heat capacities	98
3.3.2 Enthalpy, H , of pure phases as a function of temperature	101
3.4 Enthalpy of solutions	106
3.4.1 Enthalpy of binary solution	107
3.4.2 Examples of enthalpy of mixing in binary solutions	110
3.5 Enthalpy of reaction	116
3.5.1 Temperature dependence of the enthalpy of reaction	119
3.5.2 Hess's law	122
3.6 Problems	124
 Chapter 4 Second law of thermodynamics	129
4.1 Entropy	130
4.2 Classical definition of entropy	130
4.2.1 Entropy of pure phases	131
4.2.2 Adiabatic changes	136
4.2.3 Temperature dependence of entropy	137
4.2.4 Entropy changes associated with irreversible processes	140
4.3 Statistical interpretation of entropy	144
4.3.1 Thermal entropy	145
4.3.2 Configurational entropy (entropy of mixing)	149
4.4 Entropy of reaction	160
4.4.1 Temperature dependence of the entropy of reaction	160
4.5 Problems	163
 Chapter 5 Gibbs free energy and Helmholtz free energy	165
5.1 Chemical potential of pure phases	168
5.1.1 Chemical potential of ideal gases	168
5.1.2 Chemical potential of non-ideal gases	169
5.2 The chemical potential of components in solutions	173
5.2.1 Chemical potential of an ideal gas in an ideal solution	176
5.2.2 Chemical potential of a real gas in ideal and non-ideal gas mixtures	177
5.2.3 Chemical potential of components in ideal solid solutions	181
5.2.4 Chemical potential of components in non-ideal solid solutions	183
Activity and activity coefficient as a function of composition	184
5.2.5 The standard state	186
The activity coefficient as a function of temperature and pressure	189
5.3 Gibbs free energy of mixing	191
5.3.1 Mixing and activity models	194
5.4 Gibbs free energy of reaction	214

5.4.1 Standard Gibbs free energy of reaction	215
5.5 Problems	216
Chapter 6 Thermal equilibrium	218
6.1 Stability conditions for phases in one-component systems	220
6.1.1 Phase equilibria in one-component systems	223
6.1.2 Classification of phase transformations	227
6.2 Stability conditions for solutions	237
6.2.1 Coherent exsolution.....	244
6.3 Gibbs free energy and phase diagrams of binary systems	249
6.3.1 Calculation of phase diagrams from thermodynamic data	253
Critical mixing conditions, binodal, spinodal.....	253
Simple eutectic system	259
Binary system with complete miscibility of the components in two phases	265
6.4 Gibbs phase rule	272
6.5 Problems	275
Chapter 7 Chemical reactions	277
7.1 Phase equilibria in reacting systems	277
7.1.1 Reactions in systems containing pure solid phases.....	278
7.1.2 Reactions in systems containing solid solutions	288
7.1.3 Reactions in systems containing solid and gas phases	291
7.1.4 Distribution coefficient, K_D	306
Reciprocal solutions.....	313
Energetics of order-disorder	325
7.2 Problems	339
Chapter 8 Geothermometry and geobarometry	343
8.1 Exchange geothermometers	345
8.2 Solvus thermometry	349
8.3 Solid-solid reactions	354
8.3.1 Reactions in one-component system	354
8.3.2 Reactions in multicomponent systems	355
8.4 Reactions involving gaseous phases	358
Solutions to problems	365
References	371
Subject Index	381