

# Contents

<b>1 Basic laws of thermodynamics</b>	<b>1</b>
1.1 First law of thermodynamics	2
1.1.1 Basic definitions	2
1.1.2 Implications of the first law of thermodynamics	4
1.1.3 Ideal gas	6
1.1.4 Thermochemistry	8
1.2 The second law of thermodynamics	12
1.2.1 Thomson and Clausius postulates	12
1.2.2 Reversible and irreversible processes	14
1.2.3 Carnot cycle	15
1.2.4 The Clausius inequality	17
1.2.5 Entropy	19
1.2.6 Implications of the second law of thermodynamics	21
1.3 The third law of thermodynamics	23
1.3.1 Nernst heat theorem	23
1.3.2 Determination of the absolute entropy	24
1.4 Helmholtz and Gibbs free energies	25
1.4.1 Direction of spontaneous processes at constant temperature	25
1.4.2 Dependence of the Helmholtz and Gibbs free energies on $p$ , $T$ , and $V$	26
1.5 Thermodynamics of open systems	30
1.5.1 Chemical potential	30
1.5.2 Conditions for equilibrium	32
<b>2 Phase equilibria I</b>	<b>35</b>
2.1 Gibbs phase rule	35
2.2 Clausius–Clapeyron equation	37
<b>3 Thermodynamic theory of solutions</b>	<b>41</b>
3.1 Thermodynamic description of solutions	41
3.2 Ideal dilute solutions	45
3.2.1 Thermodynamic functions	46
3.2.2 Boiling point	51
3.2.3 Freezing point	53
3.2.4 Solute partitioning	55
3.2.5 Composition of a saturated solution	56
3.3 Ideal solutions	57
3.4 Non-ideal solutions	59

## Contents

3.4.1	Activity	59
3.4.2	Experimental determination of activity	63
3.5	Regular solutions	64
3.6	Athermal solution model	67
3.7	Ionic solutions	69
<b>4</b>	<b>Phase equilibria II</b>	<b>74</b>
4.1	Phase diagrams of two-component systems	74
4.2	Type I phase diagrams	75
4.3	Type II phase diagrams	79
4.4	Type III phase diagrams	81
4.5	Type IV phase diagrams	83
4.6	Type V phase diagrams	84
4.7	Type VI phase diagrams	84
4.8	Labeling of one-and two-component regions of a phase diagram	85
<b>5</b>	<b>Thermodynamics of chemical reactions</b>	<b>89</b>
5.1	Thermodynamic considerations for chemical reactions	89
5.2	Thermodynamics of reactions of gases	91
5.3	Thermodynamics of reactions of pure condensed substances	94
5.4	Thermodynamics of reactions with solutions	95
<b>6</b>	<b>Interfacial phenomena</b>	<b>98</b>
6.1	Adsorption of gases	99
6.1.1	Langmuir isotherm	99
6.1.2	BET theory for multilayer adsorption	102
6.1.3	Capillary condensation	106
6.2	Gibbs interfacial thermodynamics	108
6.3	Guggenheim and Zhuhovitsky models	114
<b>7</b>	<b>Thermodynamics of stressed systems</b>	<b>117</b>
7.1	Small deformations of solids	117
7.1.1	Strain tensor	117
7.1.2	Stress tensor	120
7.2	Free energy of strained solids	122
7.3	Hooke's law	124
7.3.1	Hooke's law for anisotropic solids	124
7.3.2	Hooke's law for isotropic solids	125
7.4	Relationship between deformation and change of temperature	128
7.5	Equilibrium of stressed solids	130
7.6	Surface stress	131
<b>8</b>	<b>Kinetics of homogeneous chemical reactions</b>	<b>134</b>
8.1	Formal kinetics of homogeneous reactions	134
8.1.1	Chemical reaction rate	134
8.1.2	Determination of the reaction order and the rate constant	137

8.1.3	Kinetics of chemical reactions near equilibrium	140
8.1.4	Dependence of the rate constant on temperature	141
8.2	Kinetics of complex reactions	144
8.2.1	Kinetics of consecutive reactions	144
8.2.2	Kinetics of parallel reactions	146
8.2.3	Kinetics of chain reactions	147
<b>9</b>	<b>Thermodynamics of irreversible processes</b>	152
9.1	Onsager's first postulate	152
9.2	Onsager's second postulate	153
9.3	Thermodynamic forces for the transport of heat and matter	154
9.4	Thermodynamic forces for chemical reactions	156
9.5	Onsager's third postulate—the principle of detailed balance	158
9.6	Redefinition of the thermodynamic force	161
9.7	Procedure for the solution of irreversible thermodynamics problems	163
<b>10</b>	<b>Diffusion</b>	165
10.1	Mathematical description of diffusion	165
10.1.1	Fick's first law	166
10.1.2	Fick's second law	167
10.1.3	Several useful solutions of the one-dimensional diffusion equation	168
10.2	Diffusion as a random walk process	173
10.3	Diffusion in metals	175
10.3.1	Main experimental results	175
10.3.2	Diffusion mechanisms in metals	177
10.4	Diffusion in amorphous metals	180
10.5	Diffusion in polymers	182
10.6	Diffusion in multiphase systems	183
10.7	Thermal diffusion	186
<b>11</b>	<b>Kinetics of heterogeneous processes</b>	189
<b>12</b>	<b>Introduction to statistical thermodynamics of gases</b>	192
12.1	Gibbs statistics	192
12.2	Statistical thermodynamics of an ideal gas	197
12.2.1	Partition function of an ideal gas	197
12.2.2	Effect of translation motion of gas molecules	200
12.2.3	Energy of diatomic molecules	201
12.2.4	Rotational contributions to thermodynamic functions	203
12.2.5	Vibrational contributions to thermodynamic functions	205
12.2.6	Polyatomic molecular gasses	207

## Contents

12.2.7	Electronic contributions to thermodynamic functions	209
12.2.8	Maxwell distribution	210
12.2.9	Collisions of gas molecules with a surface	212
12.2.10	Collisions of gas molecules	213
12.2.11	Cross-sections	216
12.3	Statistical theory of chemical reactions	218
12.3.1	Calculation of the equilibrium constant from spectroscopic data	218
12.3.2	Theory of active collisions	219
12.3.3	Theory of the activated complex	221
12.3.3.1	Reaction path	222
12.3.3.2	Calculation of the rate constant	223
12.3.3.3	Theory of the activated complex versus the Arrhenius law	227
12.3.3.4	Thermodynamic form of the theory of the activated complex	228
<b>13</b>	<b>Introduction to statistical thermodynamics of condensed matter</b>	<b>230</b>
13.1	Introduction to liquid theory	230
13.1.1	Correlation functions	230
13.1.2	Determination of thermodynamic properties	232
13.1.3	Equation of state of non-crystalline matter	235
13.1.4	Born–Green–Bogoliubov equation	237
13.2	Theory of non-ideal gases	240
13.2.1	Van der Waals equation of state	240
13.2.2	Critical point	242
13.2.3	Principle of corresponding states	244
13.2.4	Fugacity	244
13.3	Statistical thermodynamics of solids	248
13.3.1	Lattice vibrations	248
13.3.2	Low temperature limit	248
13.3.3	High temperature limit	251
13.3.4	Debye’s interpolation	251
13.4	Statistical thermodynamics of solutions	254
13.4.1	Ideal dilute solutions	254
13.4.2	Substitutional solutions	255
13.4.2.1	Basic assumptions	256
13.4.2.2	Ideal solutions	257
13.4.2.3	Regular solutions	258
13.4.2.4	Theory of regular solutions: 0th approximation	260
13.4.2.5	Theory of regular solutions: 1st approximation	261
13.4.3	Interstitial solutions	265
13.4.4	Dilute ionic solutions	266

<b>Contents</b>	<b>xiii</b>
<b>Appendices</b>	<b>274</b>
Appendix I Working with partial derivatives	274
Appendix II Tensors	275
Appendix III Continuity equation	278
Appendix IV Functions $\text{erf}(z)$ and $F(z)$	279
Appendix V Integrals that frequently occur in statistical mechanics	279
<b>Example problem solutions</b>	<b>281</b>
<b>Index</b>	<b>325</b>