

# Contents

List of figures	9
<b>1 Thermodynamic background</b>	<b>13</b>
1.1 Introduction . . . . .	13
1.2 The principles . . . . .	16
1.3 Other thermodynamic state functions . . . . .	25
1.4 Qualitative relationships between thermodynamic and molecular properties . . . . .	28
1.5 Multicomponent systems . . . . .	34
1.6 Membrane or osmotic equilibrium . . . . .	37
1.7 Digression about the second principle . . . . .	41
<b>Discussion topics:</b>	
Time and thermodynamics . . . . .	14
Heat and entropy transfer . . . . .	22
Microorganisms growth . . . . .	31
Transport against concentration gradient or active transport . . .	39
<b>Problems</b> . . . . .	42
<b>2 Molecules, statistics, and matter</b>	<b>45</b>
2.1 Properties of matter . . . . .	45
2.2 The partition function . . . . .	48
2.3 Heat capacities and equipartition of energy . . . . .	50
2.4 Heat capacity of solids . . . . .	51
2.5 Molecular interactions: Their origin . . . . .	56
2.6 Different types of intermolecular forces and models . . . . .	58
2.7 Electrostatic interactions in vacuum . . . . .	59
2.8 Dispersion forces, Lennard-Jones potential . . . . .	61
2.9 The second virial coefficient . . . . .	63

2.10 Interactions between molecular aggregates . . . . .	66
2.11 Entropy and information . . . . .	68
2.12 The third principle of thermodynamics . . . . .	70
<b>Discussion Topics:</b>	
The case of water . . . . .	72
Third principle and internal molecular rotations . . . . .	73
<b>Problems</b> . . . . .	77
<b>3 Partial molar properties and phase transitions</b>	<b>81</b>
3.1 Euler's integration method for extensive properties . . . . .	81
3.2 Gibbs-Duhem's relation and the phase rule . . . . .	84
3.3 Phase equilibrium in pure substances . . . . .	86
3.4 Cubic equations of state. The van der Waals equation . . . . .	89
3.5 Metaestability and glass transition . . . . .	96
3.6 Effect of pressure on the vapor pressure of a condensed phase . . . . .	104
<b>Discussion Topics:</b>	
State equation of an elastomer . . . . .	92
Superheated liquid water . . . . .	99
<b>Problems</b> . . . . .	105
<b>4 Gaseous mixtures</b>	<b>107</b>
4.1 The chemical potential . . . . .	107
4.2 Meaning and molecular consequences of the mixing process . . . . .	108
4.3 Mixture of real gases: Fugacity and standard state . . . . .	111
4.4 Second virial coefficient and real gaseous mixtures . . . . .	114
4.5 Mixture quantities and excess functions . . . . .	117
4.6 Ideal and real gaseous mixtures . . . . .	120
<b>Discussion Topics:</b>	
Enthalpies of gaseous mixtures and determination of second virial coefficients . . . . .	118
<b>Problems</b> . . . . .	124
<b>5 Mixtures in condensed phases and their equilibrium with the vapor</b>	<b>127</b>
5.1 Ideal behavior . . . . .	127
5.2 Chemical potential in an ideal liquid mixture . . . . .	129
5.3 Mixtures of real liquids and standard states . . . . .	131

5.4 Lattice model. Simple and regular solutions . . . . .	134
5.5 Behavior of mixtures: Thermodynamic requirements . . . . .	137
5.6 Systems with azeotropes . . . . .	141
5.7 Partial immiscibility . . . . .	144
5.8 van Laar's equation . . . . .	149
5.9 Solutions of polymers and macromolecules . . . . .	151
5.10 Solubility of non-ionic solids . . . . .	155
<b>Discussion Topics:</b>	
Effect of long-lasting contaminants in the environment . . . . .	157
<b>Problems</b> . . . . .	162
<b>6 Solutions</b>	<b>167</b>
6.1 Introduction . . . . .	167
6.2 Supercritical extraction . . . . .	168
6.3 Solubility of gases in liquids . . . . .	169
6.4 Ionic solutes . . . . .	171
6.5 Some differences evidenced by ionic systems . . . . .	173
6.6 Debye-Hückel model . . . . .	176
6.7 Concentrated solutions of electrolytes . . . . .	180
6.8 Partial phase equilibrium or osmotic equilibrium . . . . .	182
6.9 Depression of the melting point and ebullioscopic elevation . . . . .	185
6.10 Osmotic pressure . . . . .	187
6.11 Determination of mean activity and osmotic coefficients . . . . .	194
<b>Discussion Topics:</b>	
The osmotic pump . . . . .	189
<b>Problems</b> . . . . .	197
<b>7 Surface phenomena</b>	<b>201</b>
7.1 Introduction . . . . .	201
7.2 Thermodynamic description of the role of surfaces . . . . .	203
7.3 Curved surfaces. Bubbles and drops . . . . .	209
7.4 Solid-gas interface. Adsorption . . . . .	212
7.5 Microheterogeneous systems: Phase formation and molecular aggregation . . . . .	220
<b>Problems</b> . . . . .	231

<b>8 Chemical equilibrium</b>	<b>235</b>
8.1 Its characteristic features	235
8.2 Homogeneous equilibrium and Variation of $G$ with the extent of reaction	239
8.3 van't Hoff's isotherm and chemical equilibrium in real systems	241
8.4 Heterogeneous chemical equilibria	243
8.5 Le Chatelier's principle and thermodynamic stability	245
8.6 A few consequences of the Le Chatelier's principle	250
8.7 Equilibrium constants and statistical mechanics	261
<b>Discussion Topics:</b>	
Equilibrium state, thermodynamics, and kinetics of chemical reactions	247
Geothermometers and geobarometers	258
<b>Problems</b>	264
<b>9 Processes with charge transfer</b>	<b>269</b>
9.1 Introduction	269
9.2 Debye-Hückel model	269
9.3 The conductivity of electrolytes	275
9.4 Charged interfaces. The electrochemical potential	278
9.5 Galvanic cells	282
9.6 Determination of mean activity coefficients and equilibrium constants	284
9.7 Colloidal systems	286
<b>Discussion Topics:</b>	
Donnan effect and membrane potential	289
<b>Problems</b>	291
<b>10 Non-Equilibrium thermodynamics and transport processes</b>	<b>295</b>
10.1 Introduction	295
10.2 The local equilibrium hypothesis	297
10.3 The continuity equation	298
10.4 The entropy production	303
10.5 Transport processes	304
10.6 Generalization of Le Chatelier's (or moderation) principle	307
10.7 Transport in homogeneous systems	308
10.8 Transport in heterogeneous systems	311

<b>Discussion topics:</b>	
Alternative description of chemical reactions	306
Controlled drug delivery	315
<b>Problems</b>	317
<b>11 Future developments</b>	<b>321</b>
11.1 Behavior of matter in temporal and spatial micro- and nanoscopic scales	321
11.2 Behavior of systems which follow the laws of thermodynamics when symmetry is broken	328
<b>Appendixes</b>	<b>333</b>
<b>A Mathematical tools</b>	<b>333</b>
<b>Discussion Topics:</b>	
Mnemonic scheme to calculate the derivatives of the derivatives of thermodynamic fundamental functions	335
The velocity of propagation of sound and thermodynamic properties	339
<b>B Tabulation and calculation of standard thermodynamic quantities</b>	<b>341</b>
<b>C Books suggested for consultation</b>	<b>345</b>
<b>Index</b>	<b>347</b>
<b>Credits</b>	<b>351</b>