

Contents

Preface to Revised Edition	vii
Preface to the First Edition	ix
Notation	xvii
Acknowledgements and Credits	xxi
1. Background	1
1.1 Introduction	1
1.2 The building blocks	3
1.3 The periodic table	5
1.4 Isotopes	5
1.5 Molecules	6
1.6 The mole	8
1.7 Waves	8
1.8 Electromagnetic radiation	10
1.9 The perfect gas	11
1.10 Chemical equilibrium	12
1.11 Ionic equilibria	14
1.12 The next steps	16
2. Energy	17
2.1 Kinetic and potential energy	17
2.2 Kinetic theory of gases	19
2.3 Equipartition of energy	21
2.4 Heat and work	23
2.5 Conservation of energy — The First Law	25
2.6 State functions	25
2.7 Enthalpy	27

Basic Physical Chemistry Revised Edition

2.8	Hess's law	29
2.9	Calorimetry	31
2.10	Coulombic energy	33
2.11	Summary of key principles	35
3.	The First Principle: Energy is Not Continuous	37
3.1	The failures of classical physics	37
3.2	Basic ideas of quantum mechanics	39
3.3	The uncertainty principle	42
3.4	Summary of important principles	43
3.5	Translational motion: Particle in a box	44
3.6	Rotational motion	48
3.7	Vibrational motion	50
3.8	The hydrogen-like atom	51
3.9	Hydrogen atom spectra	53
3.10	The Schrödinger wave equation	56
3.11	Quantum mechanics — further considerations	58
4.	Electrons in Atoms	61
4.1	Limitations of the simple model	61
4.2	Solution of the Schrödinger equation for many-electron atoms	61
4.3	Electron spin	63
4.4	Many-electron atoms	64
4.5	Pauli exclusion principle and the Aufbau principle	66
4.6	The shielding of outer electrons and atomic properties	69
4.7	Estimating atomic properties	74
4.8	Solving the Schrödinger equation for atoms	77
4.9	The ground state of the helium atom	78
4.10	Summary of key principles	81
5.	Chemical Bonding and Molecular Structure	83
5.1	The chemical bond — a historical digression	83
5.2	Valence bond theory	85
5.3	Molecular orbitals	89
5.4	Homonuclear diatomic molecules	93
5.5	Heteronuclear molecules	96
5.6	Hybridisation	97

5.7	Delocalised orbitals	100
5.8	<i>Ab initio</i> calculations	103
5.9	Summary of key principles	105
6.	Atomic and Molecular Spectra	107
6.1	Spectroscopy	107
6.2	The intensities of spectroscopic lines	110
6.3	Spectroscopic line widths	113
6.4	Atomic spectra	114
6.5	Two-electron spectra	116
6.6	Russell–Saunders coupling	118
6.7	Molecular spectra	119
6.8	Rotational spectra	120
6.9	Vibrational spectra	124
6.10	Vibrational-rotational spectra	126
6.11	Vibrations of polyatomic molecules	129
6.12	Low-resolution infrared spectra	130
6.13	Raman spectra	132
6.14	Molecular electronic spectra	133
6.15	Low-resolution electronic spectra	137
6.16	The fate of excited electronic states	139
6.17	Nuclear magnetic resonance (NMR)	140
6.18	Electron spin resonance spectroscopy	145
6.19	Summary of key principles	145
7.	The Second Principle: The Higher, the Fewer	147
7.1	Equilibrium	147
7.2	Why we need a second principle	149
7.3	The second factor	151
7.4	Microstates	152
7.5	The Boltzmann factor	153
7.6	Entropy	157
7.7	Defining the position of equilibrium	159
7.8	Entropy as a function of pressure and temperature	160
7.9	Partition functions	162
7.10	Determination of thermodynamic functions from partition functions	165
7.11	Summary of key principles	172

8. Chemical Equilibrium	175
8.1 Free energy	175
8.2 Gibbs free energy	176
8.3 The pressure and temperature dependence of Gibbs free energy	177
8.4 Chemical potential	179
8.5 Equilibrium between gaseous reactants	180
8.6 The temperature dependence of the equilibrium constant . . .	183
8.7 The effect of pressure on equilibrium constants	185
8.8 Equilibrium calculations using thermodynamic tables	187
8.9 Equilibrium constants from free energy functions	191
8.10 Equilibrium constants and partition functions	192
8.11 Summary of the basic equations of chemical thermodynamics	196
9. The States of Matter	199
9.1 Gases, liquids and solids	199
9.2 The thermodynamics of phase changes	201
9.3 Intermolecular energy	203
9.4 The origins of intermolecular energy	205
9.5 Gas imperfection	211
9.6 Critical behaviour	213
9.7 Corresponding states	214
9.8 The liquid state	215
9.9 The solid state	217
9.10 Crystal structure	218
9.11 X-ray diffraction	221
9.12 Molecular structures by diffraction methods	224
9.13 Solid surfaces	226
9.14 Summary of key principles	229
10. Mixtures and Solutions	231
10.1 The ideal solution	231
10.2 Truly ideal solutions	233
10.3 Ideal solutions of solids in liquids	235
10.4 Ideal dilute solutions	237
10.5 Non-ideal solutions	241
10.6 Molecular basis of ideality	243
10.7 Ions in solution	245

10.8	Debye–Hückel theory	246
10.9	Electrochemical cells	249
10.10	Summary of key principles	252
11.	Rates of Chemical Reactions	255
11.1	The order of reactions	255
11.2	First-order reactions	256
11.3	Second-order reactions	258
11.4	Determination of reaction order	259
11.5	Effect of temperature on reaction rates	260
11.6	Collision theory	261
11.7	Activated complex theory	264
11.8	Thermodynamic interpretation of activated complexes	268
11.9	Unimolecular reactions	269
11.10	Chain reactions	272
11.11	Explosions	275
11.12	Reactions in solution	277
11.13	Catalysis	278
11.14	Reaction dynamics	282
11.15	Photochemical reactions	284
11.16	Summary of key principles	286
Answers to Problems		289
Appendix 1 Thermochemical Data at 298.15 K		290
Appendix 2 Hydrogen-Like Wave Functions		292
Appendix 3 Symmetry		294
Appendix 4 Units and Fundamental Constants		295
Further Reading		297
The Periodic Table		299
Index		301