

# Contents

<b>Chapter 1. Introduction</b>	<b>1</b>
1-1 Theory and experiment	1
1-2 Physical inorganic chemistry	2
(a) Structure	2
(b) The process of reaction	6
1-3 Reference literature	8
<b>Chapter 2. Ionic crystals</b>	<b>9</b>
2-1 The nature of the crystalline state	9
2-2 Crystal structures of some simple salts	12
(a) The sodium chloride structure	12
<b>(b) The cesium chloride structure</b>	<b>14</b>
(c) The fluorite structure	15
(d) The rutile structure	16
2-3 The existence of ions	17
(a) Ionic radii	19
(b) Theoretical significance of ionic radii	24
2-4 Bonding forces in ionic crystals	25
(a) Crystal energies of the alkali halides	27
(b) Crystal energies of other ionic compounds	35
2-5 Crystal energies and physical and chemical properties	36
(a) Melting and boiling points of the alkali halides	36
(b) Factors governing the coordination number	40
<b>Chapter 3. Atomic structure</b>	<b>45</b>
3-1 Atomic spectra	46
(a) The hydrogen atom spectrum	46
(b) Spectra of other atoms	48
3-2 Atomic structure and atomic spectra	50
(a) The Bohr postulates	51
(b) The classical treatment of physical problems	54
3-3 Wave mechanics	56
(a) The wave nature of the electron	57
<b>(b) The Schrödinger equation</b>	<b>58</b>

3-4	Wave mechanics of the hydrogen atom . . . . .	62
	(a) Hydrogen atom energy levels . . . . .	63
	(b) Hydrogen atom wave functions . . . . .	65
3-5	Manyelectron atoms . . . . .	73
	(a) Basic principles of description . . . . .	73
	(b) Electron interactions; the Pauli principle . . . . .	75
	(c) The Aufbau principle and the periodic table . . . . .	77
	(d) Wave functions for many-electron atoms . . . . .	83
	(e) Electronic configuration and <b>periodic</b> properties . . . . .	88
<b>Chapter 4. Thermochemistry . . . . .</b>		<b>96</b>
4-1	Heat and energy . . . . .	97
4-2	Heats of formation . . . . .	98
4-3	Hess' law . . . . .	99
	(a) Some applications of Hess' law . . . . .	101
	(b) Stability . . . . .	104
4-4	Bond energies . . . . .	105
	(a) Bond dissociation energies . . . . .	106
	(b) Bond energies . . . . .	108
	(c) Estimation of thermochemical data . . . . .	111
<b>Chapter 5. Molecular structure . . . . .</b>		<b>115</b>
5-1	Symmetry and empirical considerations . . . . .	116
	(a) <b>Symmetry and coordination</b> . . . . .	116
	(b) Methods of structure determination . . . . .	122
	(c) Bond lengths . . . . .	132
5-2	Diatomic molecules . . . . .	137
	(a) The hydrogen molecule; MO approximation . . . . .	137
	(b) The hydrogen molecule; VB approximation . . . . .	143
	(c) <b>Homonuclear</b> diatomic molecules; MO treatment . . . . .	146
	(d) Homonuclear diatomic molecules; VB treatment . . . . .	153
	(e) Heteronuclear diatomic molecules . . . . .	156
5-3	Polyatomic molecules . . . . .	163
	(a) Localized orbitals and the overlap criterion . . . . .	164
	(b) Hybridization . . . . .	165
	(c) Directed valency in the second period . . . . .	170
	(d) Multiple bonding and delocalized orbitals . . . . .	175
	(e) Structure of more complex molecules . . . . .	189
<b>Chapter 6. Transition metal complexes . . . . .</b>		<b>203</b>
6-1	Introduction . . . . .	203
6-2	Stereochemistry of transition metal complexes . . . . .	204
	(a) <b>Geometrical isomerism</b> . . . . .	206
	(b) Structural isomerism . . . . .	209
6-3	Nomenclature . . . . .	210
6-4	Bonding in transition metal complexes . . . . .	213
	(a) Valence-bond theory . . . . .	214
	(b) Crystal-field theory . . . . .	218
	(c) Ligand-field theory . . . . .	222

<b>Chapter 7. Crystal chemistry</b>	<b>234</b>
7-1 The classification and description of crystals	234
(a) Symmetry and space lattices	234
(b) Classification according to bonding or structure type	239
7-2 Molecular crystals	241
(a) Close packing of spheres	241
(b) Simple molecular crystals	244
(c) Intermolecular forces and hydrogen bonding	250
7-3 Metals	258
(a) Structure of pure metals	260
(b) Simple alloys	261
(c) Interstitial compounds	263
(d) Bonding in metals.	265
7 4 Covalent crystals	268
7-5 Ionic and intermediate types of crystals	271
(a) Van der Waals and covalent bonding in ionic crystals	272
(b) Crystal chemistry of the transition metals	275
(c) Complex ions in crystals	278
(d) Silicates	279
<b>Chapter 8. Thermodynamics</b>	<b>284</b>
8-1 Equilibrium	284
(a) Quantitative aspects of equilibrium	286
8-2 Effect of temperature on equilibria	290
8-3 Entropy	295
(a) Temperature dependence of entropy and enthalpy	298
(b) Trends in entropies	302
(c) Molecular basis of entropy	307
8 4 Free energy	310
(a) Thermodynamic activity	313
<b>Chapter 9. Solutions of electrolytes</b>	<b>316</b>
9-1 Nature of electrolytic solutions	316
(a) Ionic equilibria and activity	317
(b) Thermodynamic properties	321
9-2 Hydration	324
(a) Enthalpy of hydration	325
<b>(b) Entropy of hydration</b>	<b>328</b>
(c) Theoretical treatment of hydration	330
9-3 Acids and bases	335
(a) Acid and base' strength	336
(b) Trends in acidities	340
(c) Aprotic acids and bases	345
9 4 Complex ions	346
(a) Trends in stability.	348
(b) Chelates	353
9-5 Hydrolytic equilibria	355
9-6 Oxidation and reduction	356

(a) Electrochemical cells . . . . .	357
(b) Electrode potentials . . . . .	360
(c) Concentration dependence of electrode potentials . . . . .	365
<b>Chapter 10. Rates and mechanisms of reactions . . . . .</b>	<b>373</b>
<b>10-1 Reaction kinetics . . . . .</b>	<b>373</b>
(a) Mechanisms of reaction . . . . .	376
<b>(b) Temperature dependence of the rate constant . . . . .</b>	<b>378</b>
(c) Theoretical treatment of rate constants . . . . .	380
<b>10-2 Gas-phase reactions . . . . .</b>	<b>382</b>
<b>10-3 Acid-base reactions . . . . .</b>	<b>384</b>
<b>10-4 Substitution reactions . . . . .</b>	<b>388</b>
(a) Mechanisms for hydrolysis reactions . . . . .	389
(b) Mechanisms for <b>anation</b> reactions . . . . .	392
(c) Mechanisms for other substitution reactions . . . . .	392
<b>10-5 Oxidation-reduction reactions . . . . .</b>	<b>394</b>
(a) One electron reactions . . . . .	394
(b) Two electron reactions . . . . .	398
(c) Noncomplementary reactions . . . . .	400
(d) Free radical reactions. . . . .	401
<b>Appendix I . . . . .</b>	<b>403</b>
Appendix II . . . . .	404
Formula Index . . . . .	415
List of Symbols . . . . .	423
Index . . . . .	429