

# Contents

Preface	v
Acknowledgements	vii
1. Atomic Structure and the Periodic Table	1
1.1 The Subatomic Particles of Matter . . . . .	1
1.1.1 Behaviour in an electric field/magnetic field . . . . .	1
1.1.2 Isotopes . . . . .	3
1.1.3 Relative masses of an element . . . . .	4
1.2 Orbitals and Quantum Numbers . . . . .	6
1.2.1 The nature of electron . . . . .	6
1.2.2 Shapes of orbitals . . . . .	10
1.3 Electronic Configurations . . . . .	12
1.3.1 Rules used in working out electronic configuration . . . . .	12
1.3.2 Electronic configuration of transition elements . . . . .	15
1.3.3 Anomalous electronic configurations . . . . .	16
1.4 Ionisation Energies . . . . .	16
1.4.1 Factors influencing the magnitude of ionisation energies . . . . .	17
1.5 Periodic Table: Trend in Ionisation Energy . . . . .	22
1.6 Periodic Table: Trend in Atomic Radii . . . . .	24
2. Chemical Bonding	29
2.1 Metallic Bonding . . . . .	29
2.1.1 Physical properties of metals . . . . .	30
2.2 Ionic Bonding (or Electrovalent Bonding) . . . . .	31
2.2.1 Guidelines for drawing dot-and-cross diagrams . . . . .	34
2.2.2 Physical properties of ionic compounds . . . . .	35

2.3	Covalent Bonding . . . . .	39
2.3.1	Covalent bond formation . . . . .	40
2.3.2	Dative covalent bond (coordinate bond) . . . . .	42
2.3.3	Factors affecting strength of covalent bond . . . . .	44
2.3.4	Shapes of molecules — The VSEPR model . . . . .	46
2.3.5	Using the Hybridisation Model to understand shape . . . . .	52
2.3.6	Delocalised bonding/resonance . . . . .	56
2.4	Intermediate Bond Types . . . . .	58
2.4.1	Covalent character in ionic bonds . . . . .	58
2.4.2	Ionic character in covalent bonds . . . . .	60
2.5	Physical Properties of Covalent Compounds . . . . .	62
2.5.1	Properties of giant covalent compounds . . . . .	62
2.5.2	Properties of simple covalent compounds . . . . .	64
2.6	Intermolecular Forces of Attraction . . . . .	64
2.6.1	Instantaneous dipole–induced dipole (id–id) interactions . . . . .	65
2.6.2	Permanent dipole–permanent dipole (pd–pd) interactions . . . . .	67
2.6.3	Hydrogen bonding . . . . .	70
2.7	Summary of Chemical Bonding: Putting it all Together . . . . .	74
3.	Ideal Gas and Gas Laws . . . . .	81
3.1	Gas Laws . . . . .	82
3.1.1	Boyle’s law . . . . .	82
3.1.2	Charles’ law . . . . .	83
3.1.3	Gay-Lussac’s law . . . . .	84
3.1.4	Avogadro’s law . . . . .	84
3.1.5	The ideal gas law . . . . .	88
3.1.6	Further manipulations of the ideal gas equation . . . . .	90
3.1.7	Dalton’s Law of Partial Pressure . . . . .	91
3.1.8	Types of mathematical problems involving the gas laws . . . . .	95
3.2	Kinetic Theory of Gases . . . . .	96
3.2.1	Graphical plots representing ideal behaviour . . . . .	97
3.2.2	Deviation from ideal gas behaviour . . . . .	100
3.2.3	Nature of gas . . . . .	103

4.	Chemical Thermodynamics	109
4.1	Energy Changes in Chemical Reactions . . . . .	110
4.1.1	Standard enthalpy changes . . . . .	113
4.1.2	Calculating enthalpy changes from experimental data . . . . .	117
4.1.3	Calculation of enthalpy changes using Hess' Law . . . . .	122
4.1.4	Constructing energy cycles . . . . .	123
4.1.5	Born–Haber cycle and Hess' law . . . . .	127
4.1.6	Constructing Born–Haber cycles . . . . .	129
4.1.7	Energetics involving aqueous ionic compounds . . .	133
4.2	Entropy . . . . .	135
4.2.1	What is entropy? . . . . .	137
4.2.2	Factors affecting entropy of a chemical system . . .	138
4.2.3	Predicting the spontaneity of a reaction . . . . .	141
4.2.4	Relationship between $\Delta G^\circ$ , $\Delta H^\circ$ , $\Delta S^\circ$ and temperature . . . . .	142
5.	Reaction Kinetics	147
5.1	Qualitative Analysis of Reaction Rates . . . . .	147
5.1.1	Factors affecting reaction rates . . . . .	150
5.2	Quantitative Analysis of Reaction Rates . . . . .	155
5.2.1	Rate of reaction . . . . .	155
5.2.2	The rate equation (Rate law) . . . . .	159
5.2.3	Experimental methods used to determine order of reaction . . . . .	164
5.3	Rate Equation and Reaction Mechanism . . . . .	182
5.4	Transition State Theory . . . . .	184
5.5	Catalysis . . . . .	187
5.5.1	Homogeneous catalysis . . . . .	187
5.5.2	Heterogeneous catalysis . . . . .	188
5.5.3	Autocatalysis . . . . .	190
5.5.4	Enzymes (biological catalysts) . . . . .	191
6.	Chemical Equilibria	197
6.1	Reversible Reactions . . . . .	197
6.2	Equilibrium Systems . . . . .	199
6.3	Equilibrium Constants $K_c$ and $K_p$ . . . . .	200

6.3.1	Writing $K_c$ or $K_p$ for heterogeneous equilibria . . .	204
6.3.2	Calculations involving $K_c$ . . . . .	205
6.3.3	Calculations involving $K_p$ . . . . .	208
6.4	Le Chatelier's Principle . . . . .	211
6.4.1	Effect of concentration changes . . . . .	211
6.4.2	Effect of pressure changes . . . . .	214
6.4.3	Effect of temperature changes . . . . .	220
6.4.4	Effect of temperature changes on the value of the equilibrium constant . . . . .	222
6.4.5	Effect of catalyst . . . . .	223
6.5	The Haber Process . . . . .	226
7.	Ionic Equilibria . . . . .	231
7.1	The Brønsted–Lowry Theory of Acids and Bases . . . . .	232
7.2	Conjugate Acid–Base Pairs . . . . .	234
7.3	The pH Scale . . . . .	234
7.4	The Dissociation Constant of Water, $K_w$ . . . . .	235
7.5	Strength of Acids . . . . .	240
7.6	Acid Dissociation Constant $K_a$ and $pK_a$ . . . . .	241
7.7	Strength of Bases . . . . .	246
7.8	Base Dissociation Constant $K_b$ and $pK_b$ . . . . .	247
7.9	Complementary Strengths of a Conjugate Acid–Base Pair . . . . .	249
7.10	Hydration and Hydrolysis . . . . .	251
7.10.1	Classifying type of salt based on strengths of acid and base that form it . . . . .	253
7.10.2	Hydrolysis of high charge density cations . . . . .	255
7.11	Buffer Solutions . . . . .	256
7.11.1	How does an acidic buffer work . . . . .	256
7.11.2	How does an alkaline buffer work . . . . .	258
7.11.3	The role of buffer in controlling pH in blood . . . . .	259
7.11.4	Calculating pH of buffer solutions . . . . .	260
7.12	Acid–Base Indicators . . . . .	263
7.13	Acid–Base Titrations . . . . .	266
7.13.1	Titration curve of a strong acid–strong base titration . . . . .	268
7.13.2	Titration curve of a weak acid–strong base titration . . . . .	269

7.13.3	Titration curve of a strong acid–weak base titration . . . . .	276
7.13.4	Titration curve of a weak acid–weak base titration . . . . .	278
7.13.5	Titration curve of a polybasic acid–strong base titration . . . . .	280
7.13.6	Titration curve of a carbonate–strong acid titration (Double-Indicator Method) . . . . .	281
7.13.7	Titration curve of a mixture of weak acids — strong base titration . . . . .	286
7.13.8	Back-titration . . . . .	288
7.14	Solubility Product $K_{sp}$ . . . . .	290
7.14.1	Solubility and $K_{sp}$ . . . . .	291
7.14.2	Ionic product and $K_{sp}$ . . . . .	293
7.14.3	Common ion effect . . . . .	295
7.14.4	Solubility in qualitative analysis . . . . .	297
8.	Redox Chemistry and Electrochemical Cells	303
8.1	Rules for Assignment of Oxidation States . . . . .	307
8.2	Balancing Redox Equations . . . . .	310
8.3	Redox Titrations . . . . .	313
8.3.1	Manganate(VII) titrations . . . . .	314
8.3.2	Dichromate(VI) titrations . . . . .	315
8.3.3	Iodine-thiosulfate titrations . . . . .	316
8.4	Redox Reactions and Electricity . . . . .	318
8.4.1	Electrode potential . . . . .	319
8.4.2	Experimental set-up of half-cells . . . . .	322
8.4.3	Information obtained from the standard electrode potential . . . . .	325
8.4.4	Describing cell components using conventional notation . . . . .	328
8.4.5	Calculating standard cell potential . . . . .	330
8.4.6	Using $E^{\ominus}_{cell}$ to predict feasibility of a reaction . . . . .	332
8.4.7	Effect of concentration changes on $E^{\ominus}_{cell}$ value . . . . .	335
8.4.8	Effect of ligands on $E^{\ominus}_{cell}$ value . . . . .	337
8.5	Types of Electrochemical Cells . . . . .	338
8.6	Electrolysis . . . . .	341
8.6.1	Faraday's laws of electrolysis . . . . .	342

8.6.2	Selective discharge of ions . . . . .	345
8.6.3	Industrial uses of electrolysis . . . . .	347
9.	The Periodic Table — Chemical Periodicity . . . . .	357
9.1	Atomic Structure and Period 3 Elements . . . . .	359
9.1.1	Trend in atomic radius . . . . .	359
9.1.2	Trend in ionic radius . . . . .	361
9.1.3	Trend in first ionisation energy (1st I.E.) . . . . .	362
9.1.4	Trend in electronegativity . . . . .	363
9.2	Structure, Bonding and Period 3 Elements . . . . .	364
9.2.1	Variation in melting points and boiling points . . . . .	364
9.2.2	Variation in electrical conductivity . . . . .	365
9.3	Oxides and Chlorides of Period 3 Elements . . . . .	366
9.3.1	Oxides of Period 3 elements . . . . .	369
9.3.2	Chlorides of Period 3 elements . . . . .	373
10.	Chemistry of Groups 2 and 7 . . . . .	381
10.1	Atomic Structure and Group Trends . . . . .	381
10.1.1	Trend in atomic radius . . . . .	381
10.1.2	Trend in ionic radius . . . . .	382
10.1.3	Trend in 1st I.E. . . . .	382
10.1.4	Trend in electron affinity . . . . .	382
10.1.5	Trend in electronegativity . . . . .	383
10.1.6	Trend in metallic character . . . . .	383
10.2	Physical Properties of Group 2 Elements . . . . .	384
10.3	Chemical Properties of Group 2 Elements . . . . .	384
10.3.1	Reaction with water . . . . .	386
10.3.2	Reaction with oxygen . . . . .	387
10.4	Thermal Stability of Group 2 Compounds . . . . .	387
10.5	Some Uses of Group 2 Elements and Their Compounds . . . . .	391
10.6	Properties of Beryllium . . . . .	391
10.7	Solubility of Group 2 Compounds . . . . .	394
10.8	Physical Properties of Group 7 Elements . . . . .	397
10.8.1	Melting point, boiling point and volatility . . . . .	397
10.8.2	Colour . . . . .	398
10.8.3	Solubility in water . . . . .	399
10.8.4	Solubility in organic solvent . . . . .	399

10.8.5	Trend in bond energy . . . . .	400
10.9	Chemical Properties of Group 7 Elements . . . . .	400
10.9.1	Displacement reaction of halogens . . . . .	402
10.9.2	Reaction with thiosulfate . . . . .	403
10.9.3	Reaction with alkali . . . . .	406
10.9.4	Reaction with hydrogen . . . . .	408
10.10	Hydrogen Halides . . . . .	409
10.10.1	Thermal stability of hydrogen halides . . . . .	410
10.10.2	Acidity of hydrogen halides . . . . .	411
10.10.3	Reaction of halides with concentrated acid . . . . .	411
10.10.4	Distinguishing tests for halide ions . . . . .	413
10.11	Industrial Uses and Environmental Impact of Group 7 Elements and Their Compounds . . . . .	415
10.11.1	Fluorine and its compounds . . . . .	415
10.11.2	Chlorine and its compounds . . . . .	415
10.11.3	Bromine and its compounds . . . . .	415
11.	Introduction to Transition Metals and Their Chemistry	421
11.1	Writing Electronic Configuration . . . . .	422
11.2	Physical Properties of Transition Metals . . . . .	425
11.2.1	Trend in atomic radius . . . . .	425
11.2.2	Trend in ionic radius . . . . .	426
11.2.3	Trend in first ionisation energy . . . . .	427
11.2.4	Trend in melting and boiling points . . . . .	428
11.2.5	Trend in electrical conductivity . . . . .	429
11.2.6	Trend in density . . . . .	429
11.3	Chemical Properties of Transition Metals . . . . .	430
11.3.1	Variable oxidation states . . . . .	430
11.3.2	Catalytic properties . . . . .	434
11.3.3	Formation of complexes . . . . .	437
11.3.4	The property of colour . . . . .	444
11.3.5	Ligand exchange reactions . . . . .	451
11.3.6	Selected reactions of some transition metals and their compounds . . . . .	458