

Contents

	Preface	xii
Chapter 1	Atomic structure and chemical bonding	1
1.1	The electronic structure of atoms	1
1.2	The periodic table	3
1.3	The directional properties of orbitals	6
1.4	Ionic bonding	7
1.5	Covalent bonding	10
	1.5.1 Formation of sigma bonds	10
	1.5.2 Electronegativity	11
	1.5.3 Bonding and structure in polyatomic molecules	12
	1.5.4. Rotation about single (σ) bonds	15
	1.5.5. The coordinate bond (dative covalent bond)	18
	1.5.6 Multiple bonds	21
	1.5.7 Delocalization of π bonds and resonance	22
1.6	The hydrogen bond	26
1.7	Radioactivity	28
	1.7.1 Radioactive disintegration	28
	1.7.2 Detection, measurement and applications of radio- activity	31
Chapter 2	The structural theory of organic chemistry	35
2.1	Introduction	35
2.2	Empirical, molecular, and constitutional formulae	35
2.3	The arrangement of carbon atoms	37
2.4	Functional groups in organic compounds	40
2.5	Constitutional isomerism	40
2.6	The nomenclature of organic compounds	43
2.7	Further types of isomerism	46
	2.7.1 Tautomerism	46
	2.7.2 Stereoisomerism	47
2.8	Optical isomerism and molecular dissymmetry	48
	2.8.1 Dissymmetry, asymmetric carbon atoms and enantiomorphs	48
	2.8.2 Relative and absolute configuration	49

2.8.3	Correlations using the D/L convention	52
2.8.4	The sequence rule	54
2.8.5	Compounds with two or more asymmetric carbon atoms	55
2.8.6	Separation of mixtures of enantiomorphs	57
2.9	Geometrical isomerism in unsaturated compounds	58
2.10	Stereoisomerism in cyclic compounds	61
2.11	Conformation of open-chain and cyclic molecules	62
Chapter 3	Physical aspects of chemical reactions (The thermodynamics (energetics) and kinetics of chemical reactions)	67
3.1	Introduction	67
3.2	The mathematical characterization of the first law of thermodynamics	67
3.3	Heats of reaction at constant volume and constant pressure	68
3.4	The enthalpy or heat content H and heats of reaction	70
3.4.1	Standard heats of formation	70
3.4.2	Hess's law of heat summation	71
3.4.3	Heats of combustion	72
3.4.4	Heats of neutralization, heats of solution and heats of dilution	72
3.4.5	The temperature dependence of enthalpy and heat of reaction (the Kirchhoff equation)	74
3.4.6	Bond energies	75
3.5	Free energy, available energy and chemical potential	75
3.6	Entropy and the second law of thermodynamics	80
3.7	Entropy changes in physical processes	82
3.8	Some further useful thermodynamic equations	83
3.9	The rates of chemical reactions	84
3.9.1	The limitations of chemical thermodynamics and factors affecting the rate of a reaction	84
3.9.2	Stoichiometry, order of reaction, rate equation, and molecularity	85
3.9.3	The measurement of the rate of reaction	87
3.9.4	The mathematical characterization of simple kinetic systems	92
3.9.5	The evaluation of the order of a reaction	93
3.9.6	The effect of temperature on the rate of reaction	95
3.9.7	Thermodynamic formulation of reaction rates	97
3.9.8	Homogeneous chemical catalysis	98
Chapter 4	The reactions of organic molecules	103
4.1	Physical aspects of organic reactions	103

4.1.1	Organic reaction mechanisms	103
4.1.2	The mechanisms of electron displacement in covalent bonds	105
4.2	Acidic and basic properties in organic molecules	107
4.2.1	Acidic properties	107
4.2.2	Basic properties	108
4.3	Nucleophilic substitution	110
4.3.1	Nucleophilic substitution at a saturated carbon atom	110
4.3.2	Mechanism of nucleophilic substitution	111
4.4	Substitution in aromatic compounds	113
4.4.1	The mechanism of some common substitution reactions of benzene	113
4.4.2	Electrophilic substitution in heterocyclic compounds	116
4.4.3	Nucleophilic substitution in aromatic compounds	117
4.4.4	Aromatic substitution in biochemical reactions	118
4.5	Addition reactions	118
4.5.1	Nucleophilic addition	119
4.5.2	Electrophilic addition	121
4.5.3	Addition reactions in more complex molecules	123
4.5.4	Carbon-carbon bond formation with aldehydes and ketones	125
4.6	The formation of carbon-carbon double bonds	126
4.6.1	Elimination reactions	126
4.6.2	The mechanism of common elimination reactions	127
4.7	Some reactions of carboxylic acids and their esters	129
4.7.1	Reactions of substituted acids	130
4.7.2	Esters and amides	131
4.7.3	Carbon-carbon bond formation via esters	134
4.8	Free-radical reactions	134
4.9	Rearrangements	136
4.9.1	Nucleophilic rearrangements	136
4.9.2	Electrophilic and free-radical rearrangements	138
4.10	Oxidation and reduction reactions	139
4.10.1	Introduction	139
4.10.2	Some oxidizing agents used in organic chemistry	140
4.10.3	Some common reducing agents used in organic chemistry	141
Chapter 5	The physical chemistry of liquids and solutions	143
5.1	Introduction to the properties of the liquid state	143
5.2	Physical properties of liquids	143

5.2.1	Density	143
5.2.2	The viscosities of liquids and suspensions	143
5.2.3	Surface tension of liquids	146
5.3	Properties of solutions of non-electrolytes	147
5.3.1	Solubility of gases in liquids	147
5.3.2	Colligative properties of solutions	149
5.3.3	Non-ideal solutions, partial molar quantities and activity	151
5.4	Properties of the solutions of electrolytes	154
5.4.1	Electrolytic dissociation, activity, and ionic strength	154
5.4.2	Applications of cryoscopy in biology and medicine	156
5.4.3	Measurement and interpretation of electrolytic conductance	157
5.4.4	Electrode potential, electrodes and potentiometric measurements including pH	162
5.4.5	Redox electrodes and redox reactions	169
5.4.6	Electroanalytical techniques	172
5.5	Membrane phenomena	176
5.5.1	Osmosis and osmotic pressure	176
5.5.2	Donnan membrane phenomena	178
5.5.3	Membrane potential and nerve-impulse transmission	183
5.6	Acid and base properties	185
5.6.1	Acid and base strength	185
5.6.2	Polyprotic acids, polyamines and amino acids	187
5.6.3	Salt hydrolysis and buffers	191
5.7	Surface phenomena	193
5.7.1	Adsorption isotherms	193
5.7.2	Surface-active agents	194
5.7.3	Electrophoresis	197
Chapter 6	Chromatography and spectroscopy	201
6.1	Chromatography	201
6.1.1	Introduction	201
6.1.2	Gas chromatography	202
6.1.3	Liquid-adsorption and liquid-liquid partition chromatography	205
6.1.4	Ion-exchange chromatography	208
6.1.5	Gel filtration	211
6.1.6	Affinity chromatography	215
6.2	Spectroscopic methods	217
6.2.1	The electromagnetic spectrum, molecular quantization and energy transitions	217

6.2.2	The Beer–Lambert law and quantitative measurement	220
6.2.3	Spectroscopic measurements in the ultraviolet, visible and infrared regions	222
6.2.4	Flame photometry and atomic absorption spectrophotometry	229
6.2.5	Fluorescence, fluorimetry and spectrofluorimetry	232
6.2.6	Nephelometry and turbidimetry	234
6.2.7	Magnetic resonance methods	236
6.2.8	Optical rotatory power	241
6.2.9	X-ray studies	246
Chapter 7	The structure and properties of some natural organic compounds	250
7.1	Amino acids	250
7.1.1	The structure and properties of α -amino acids	250
7.1.2	Polypeptide synthesis	255
7.2	Lipids	257
7.2.1	Simple lipids	257
7.2.2	Fatty acids	258
7.2.3	Complex lipids	260
7.3	Carbohydrates	265
7.3.1	Classification and structure of monosaccharides	265
7.3.2	Nitrogen-containing monosaccharides and vitamin C	273
7.3.3	The structural investigation of disaccharides	275
7.4	Nucleosides, nucleotides and nucleotide coenzymes (including B-group vitamins)	278
7.4.1	Nucleosides and nucleotides	278
7.4.2	Coenzymes containing nucleotide units and other coenzymes related to B-group vitamins	281
7.5	Fat-soluble vitamins and structurally related compounds, including steroids	291
7.5.1	Fat-soluble vitamins: lipoic acid, vitamins A, E, and K	291
7.5.2	Steroids	296
Chapter 8	The structure and properties of biopolymers	303
8.1	Physical properties and structural features of biopolymers	303
8.1.1	Macromolecules and colloids	303
8.1.2	General structural features of biopolymers	309
8.2	The properties and action of enzymes	318
8.2.1	The nature of enzyme-catalysed reactions	318

8.2.2	Structural and mechanistic interpretation of enzymic catalysis	328
8.2.3	Nomenclature and classification of enzymes	335
8.3	Polysaccharides	336
8.3.1	Structural investigation	336
8.3.2	Structural polysaccharides	338
8.3.3	Nutritional polysaccharides	344
8.4	Polypeptides and proteins	347
8.4.1	Classification	347
8.4.2	Structural determination—primary structure	348
8.4.3	Polypeptide hormones	353
8.4.4	Polypeptide antibiotics	357
8.4.5	The three-dimensional structure of proteins	360
8.4.6	Glycoproteins	367
8.5	Nucleic acids	370
8.5.1	Introduction	370
8.5.2	Deoxyribonucleic acid (DNA)	371
8.5.3	Ribonucleic acids (RNA)	376
8.5.4	Polynucleotide synthesis	384
Chapter 9	Chemical reactions in living organisms	387
9.1	Metabolic processes	387
9.2	Energy production in living organisms through carbohydrate and fat catabolism	388
9.2.1	Introduction	388
9.2.2	Formation and degradation of the glucosyl unit to pyruvate	390
9.2.3	The further catabolism of pyruvate	392
9.2.4	The phosphogluconate pathway (pentose phosphate pathway)	394
9.2.5	The oxidation of triglycerides	398
9.2.6	The tricarboxylic acid cycle	400
9.2.7	The respiratory chain and the production of ATP	401
9.3	The biosynthesis of carbohydrate and lipid	404
9.3.1	Introduction	404
9.3.2	The biosynthesis of carbohydrates in green plants	405
9.3.3	The biosynthesis of carbohydrates in animals	413
9.3.4	Control mechanisms occurring in carbohydrate metabolism	416
9.3.5	The biosynthesis of fatty acids	419
9.3.6	The biosynthesis of carbohydrate and lipids from acetyl-CoA	422

9.4	Nitrogen metabolism	427
9.4.1	Introduction	427
9.4.2	General metabolism of amino acids	428
9.4.3	The biosynthesis of pyrimidine and purine bases and the formation of nucleotides	434
9.4.4	Assimilation of inorganic nitrogen	435
9.5	The biosynthesis of nucleic acids and proteins	437
9.5.1	DNA biosynthesis	437
9.5.2	RNA biosynthesis, structure of genes and the genetic code	444
9.5.3	Protein biosynthesis	449
	Index	457