

Contents

Notes to the reader	xv
Symbols	xvii
INTRODUCTION	
1. The consequences of physics and chemistry for life	3
The constraints imposed on a biological system by its environment. The constraints imposed on a biological system by physics and chemistry. Physical chemistry and 'Biochemists'. Scope of this book.	
THE ENERGETICS OF CHEMICAL REACTIONS	
2. Basic thermodynamics	11
What is thermodynamics? Basic definitions. Statement of the first law of thermodynamics. Work and heat and internal energy. Work energy in chemical systems. The concept of enthalpy. Standard states. Enthalpy as a state function. The first law and direction of a reaction. Available energy, work and change. Statement of the second law of thermodynamics. The concept of entropy. Alternative expression of the second law of thermodynamics. The concept of free energy. Free energy and equilibrium. Thermodynamics applied to real systems. Molecular basis of enthalpy and entropy. Further reading. Problems.	
3. Chemical potential and multiple component systems	34
The concept of chemical potential. Chemical potential and change. Spontaneous reactions and equilibria. Variation of chemical potential with concentration. Dependence of ΔG on concentration. Mass action ratios and equilibrium constants. Alternative view of equilibrium constants. Variation of equilibrium constant with temperature. Dependence of enthalpy and entropy on temperature. Measurement of the thermodynamic quantities of reactions. Further reading. Problems.	
4. Binding of ligands to macromolecules	54
Ligand binding to a single site on a protein. Simultaneous binding of different ligands to a protein. A single ligand binding to multiple sites on a protein. The binding of multivalent ligands to multivalent proteins. Further reading. Problems.	

- 5. Acids, bases and pH regulation** 74
The ionic dissociation of water. The Arrhenius definition of acids and bases. The concept of pH. Conjugate acids and bases. Quantifying acid and base strengths. Relative and absolute acid and base strengths. Variation of pK_a with environment. The neutralisation of acids and bases. pH in biological systems. Buffer solutions. Quantifying buffer strengths. Regulation of pH by ion transport. Measurement of pH. Further reading. Problems.
- 6. Oxidation–reduction reactions and electrochemistry** 97
Oxidation–reduction reactions. Electrochemical cells. The thermodynamics of reversible cells. Cells and half-cells. Cell and half-cell nomenclature. Types of half-cells. Electrode potentials. The Nernst equation. Potentiometric titrations. Concentration cells. Effect of temperature on cell e.m.f. values. Calculation of thermodynamic quantities from electrochemical data. The effect of non-ideality. Coupled oxidation–reduction processes. Determination of pH. Further reading. Problems.
- 7. Chemical potentials and the properties of solutions** 122
Colligative properties. Osmosis. Osmotic pressure. Water potentials. Chemical potential of the solute. Determination of pH using permeable weak acids and bases. Equilibration of mobile solutes in the presence of charged macromolecules: the Donnan effect. Charged solutes and electric fields. Membrane potentials. Electrochemical gradients for ions. Electrochemical gradients as energy stores. Oxidative phosphorylation and photophosphorylation. Stoichiometry of proton pumping and ATP synthesis. Further reading. Problems.
- 8. Ideal and non-ideal solutions** 146
Ideal gases. Thermodynamics of ideal gases. Ideal solutions. Thermodynamics of ideal solutions. Dilute solutions. Non-ideal solutions. Thermodynamics of non-ideal solutions: effective concentrations and activity coefficients. Non-ideality in aqueous ionic solutions. Debye–Hückel theory. Comparison of the Debye–Hückel theory with experiment. Concentrated ionic solutions. Solutions of uncharged solutes. Properties of non-ideal solutions. Further reading. Problems.
- THE RATES OF CHEMICAL REACTIONS**
- 9. Basic chemical kinetics and single-step reactions** 171
Kinetics and thermodynamics. Energy profiles. Empirical observations. Reaction rate theories. Order and molecularity. Reaction half-times. Experimental determination of reaction orders and rate constants. Effect of temperature on the rate of a reaction. Effect of ionic strength on the rate of a reaction. Effect of isotopic substitution on the rate of a reaction. Further reading. Problems.
- 10. Applications of chemical kinetics to multistep reactions** 197
Parallel reactions. Reversible reactions. Consecutive reactions. The rate-determining step in consecutive reactions. The steady-state approximation in consecutive reactions. Effect of pH on the rate of a reaction. Further reading. Problems.

- 11. Catalysis and enzyme kinetics** 213
Catalysis of chemical reactions. Enzymes. Use of binding energy in catalysing single-substrate reactions. Kinetics of single-substrate enzyme reactions. Discussion of the Michaelis–Menten equation. Enzyme activities. Analysis of kinetic data. Complications to the basic rate equation. Effect of temperature on enzyme-catalysed reactions. Effect of pH on enzyme-catalysed reactions. Further reading. Problems.
- 12. Multisubstrate enzyme kinetics and enzyme inhibition** 237
Use of binding energy in catalysing multisubstrate reactions. Kinetics and mechanisms of two-substrate enzyme reactions. Enzyme inhibition. Mechanistic implications of inhibitor kinetics. Rate equations for inhibition of single-substrate enzyme reactions. Further reading. Problems.
- 13. Coupled reactions and biochemical pathways** 257
Sequential coupling of chemical reactions. Parallel coupling of chemical reactions. Coupled reactions and biochemical pathways. Kinetic control of biochemical pathways. The need for a systems-based analysis of kinetic control. Metabolic control analysis. Control coefficients. Elasticities. Further reading. Problems.
- ATOMIC AND MOLECULAR STRUCTURE**
- 14. Quantum mechanics: particles, waves and the quantisation of energy** 275
The classical picture of matter and energy. Breakdown of the classical picture. The wave–particle duality and wave-packets. Consequences of the wave-packet nature of matter. Localising waves in space gives quantisation of energy. Quantisation of energy in molecules. Occupancy of energy levels. Further reading. Problems.
- 15. Electrons in atoms** 291
Classical picture of an atom. Wave-theory model of an atom. Allowed electron orbitals and quantum numbers. Electron spin. Pauli exclusion principle. Electron energies. Electronic configurations of atoms and ions. Atomic and ionic properties. Further reading. Problems.
- 16. Bonding in molecules** 304
Definition of bonding. Types of molecular bonding. Electrons in molecules. d orbitals in transition metal complexes. d-orbital ground-state electronic configurations. Valence electron bonding in molecules. Properties of molecular bonds. Bonding in heteronuclear molecules. Bonding in multi-atom molecules. Further reading. Problems.
- 17. Interaction of molecules with electromagnetic radiation** 325
Nature of electromagnetic radiation. Absorption of electromagnetic radiation by matter. Fate of excited atoms or molecules. Basics of spectroscopy. Interpreting spectra. Further reading. Problems.

18. Non-covalent interactions and macromolecular structure	340
Non-covalent interactions between atoms. Calculating the energies of molecules. The role of solvent interactions: the hydrophobic effect. Thermodynamic stability of structured macromolecules. Cooperativity of macromolecular folding and unfolding. Further reading. Problems.	
APPENDICES	
Appendix 1. Note on units and constants	361
Appendix 2. Mathematical tools needed for this text	363
Appendix 3. Answers to problems	367
Index	397
ATOMIC AND MOLECULAR STRUCTURE	
14. Quantum mechanics: particles, waves and the quantisation of energy	355
The classical picture of matter and energy. Breakdown of the classical picture. The wave-particle duality and wave-packets. Conservation of energy and wave-packet nature of matter. Localising waves in space and quantisation of energy. Quantisation of energy in molecules. Occupancy of energy levels. Further reading. Problems.	
13. Electrons in atoms	391
Classical picture of an atom. Wave-mechanical model of an atom. Allowed electron orbits and quantum number. Electron spin. Pauli exclusion principle. Electron energies. Electronic configurations of atoms and ions. Atomic and ionic properties. Further reading. Problems.	
16. Bonding in molecules	304
Definition of bonding types of molecules. Types of bonding. Molecular orbital theory. Valence electron bonding in molecules. Properties of molecular bonds. Bonding in tetrahedral molecules. Bonding in multiple bonds. Further reading. Problems.	
17. Interaction of molecules with electromagnetic radiation	325
Nature of electromagnetic radiation. Absorption of electromagnetic radiation. Infrared spectroscopy. Microwave spectroscopy. Raman spectroscopy. Further reading. Problems.	
10. Applications	397
Nonlinear spectroscopy. Laser spectroscopy. The Franck-Condon approximation. The effect of pH on the rate of a reaction. Further reading. Problems.	