

# Summary of contents

---

Fundamentals	1
<b>PART 1</b> Equilibrium	<b>17</b>
<b>1</b> The properties of gases	19
Mathematical background 1: Differentiation and integration	42
<b>2</b> The First Law	44
Mathematical background 2: Multivariate calculus	91
<b>3</b> The Second Law	94
<b>4</b> Physical transformations of pure substances	135
<b>5</b> Simple mixtures	156
<b>6</b> Chemical equilibrium	209
<b>PART 2</b> Structure	<b>247</b>
<b>7</b> Quantum theory: introduction and principles	249
Mathematical background 3: Complex numbers	286
<b>8</b> Quantum theory: techniques and applications	288
Mathematical background 4: Differential equations	322
<b>9</b> Atomic structure and spectra	324
Mathematical background 5: Vectors	368
<b>10</b> Molecular structure	371
Mathematical background 6: Matrices	414
<b>11</b> Molecular symmetry	417
<b>12</b> Molecular spectroscopy 1: rotational and vibrational spectra	445
<b>13</b> Molecular spectroscopy 2: electronic transitions	489
<b>14</b> Molecular spectroscopy 3: magnetic resonance	520
<b>15</b> Statistical thermodynamics 1: the concepts	564
<b>16</b> Statistical thermodynamics 2: applications	592
<b>17</b> Molecular interactions	622
<b>18</b> Materials 1: macromolecules and self-assembly	659
<b>19</b> Materials 2: solids	695
Mathematical background 7: Fourier series and Fourier transforms	740
<b>PART 3</b> Change	<b>743</b>
<b>20</b> Molecules in motion	745
<b>21</b> The rates of chemical reactions	782
<b>22</b> Reaction dynamics	831
<b>23</b> Catalysis	876
Resource section	909
Answers to exercises and problems	948
Index	959

Discussion questions	130	<b>6 Chemical equilibrium</b>	<b>209</b>
Exercises	131		
Problems	132		
<b>4 Physical transformations of pure substances</b>	<b>135</b>		
<hr/>			
<b>Phase diagrams</b>	<b>135</b>	<b>Spontaneous chemical reactions</b>	<b>209</b>
<b>4.1</b> The stabilities of phases	135	<b>6.1</b> The Gibbs energy minimum	210
<b>4.2</b> Phase boundaries	137	<b>16.1</b> Impact on biochemistry: Energy conversion in biological cells	211
<b>4.3</b> Three representative phase diagrams	140	<b>6.2</b> The description of equilibrium	213
<b>14.1</b> Impact on technology: Supercritical fluids	142	<b>The response of equilibria to the conditions</b>	<b>221</b>
<b>Thermodynamic aspects of phase transitions</b>	<b>143</b>	<b>6.3</b> How equilibria respond to changes of pressure	221
<b>4.4</b> The dependence of stability on the conditions	143	<b>6.4</b> The response of equilibria to changes of temperature	223
<b>4.5</b> The location of phase boundaries	146	<b>16.2</b> Impact on technology: Supramolecular chemistry	226
<b>4.6</b> The Ehrenfest classification of phase transitions	149	<b>Equilibrium electrochemistry</b>	<b>227</b>
Checklist of key equations	152	<b>6.5</b> Half-reactions and electrodes	228
Discussion questions	152	<b>6.6</b> Varieties of cells	229
Exercises	153	<b>6.7</b> The cell potential	230
Problems	154	<b>6.8</b> Standard electrode potentials	233
		<b>6.9</b> Applications of standard potentials	235
		<b>16.3</b> Impact on technology: Species-selective electrodes	239
<b>5 Simple mixtures</b>	<b>156</b>	Checklist of key equations	240
<hr/>			
<b>The thermodynamic description of mixtures</b>	<b>156</b>	Discussion questions	241
<b>5.1</b> Partial molar quantities	157	Exercises	241
<b>5.2</b> The thermodynamics of mixing	161	Problems	243
<b>5.3</b> The chemical potentials of liquids	164		
<b>The properties of solutions</b>	<b>167</b>	<b>PART 2 Structure</b>	<b>247</b>
<b>5.4</b> Liquid mixtures	167		
<b>5.5</b> Colligative properties	169	<b>7 Quantum theory: introduction and principles</b>	<b>249</b>
<b>15.1</b> Impact on biology: Osmosis in physiology and biochemistry	175	<hr/>	
<b>Phase diagrams of binary systems</b>	<b>176</b>	<b>The origins of quantum mechanics</b>	<b>249</b>
<b>5.6</b> Vapour pressure diagrams	176	<b>7.1</b> Energy quantization	250
<b>5.7</b> Temperature–composition diagrams	179	<b>7.2</b> Wave–particle duality	255
<b>5.8</b> Liquid–liquid phase diagrams	181	<b>17.1</b> Impact on biology: Electron microscopy	259
<b>5.9</b> Liquid–solid phase diagrams	185	<b>The dynamics of microscopic systems</b>	<b>260</b>
<b>15.2</b> Impact on materials science: Liquid crystals	188	<b>7.3</b> The Schrödinger equation	260
<b>Activities</b>	<b>190</b>	<b>7.4</b> The Born interpretation of the wavefunction	262
<b>5.10</b> The solvent activity	190	<b>Quantum mechanical principles</b>	<b>266</b>
<b>5.11</b> The solute activity	191	<b>7.5</b> The information in a wavefunction	266
<b>5.12</b> The activities of regular solutions	194	<b>7.6</b> The uncertainty principle	276
<b>5.13</b> The activities of ions in solution	195	<b>7.7</b> The postulates of quantum mechanics	279
Checklist of key equations	198	Checklist of key equations	280
Further information 5.1: The Debye–Hückel theory of ionic solutions	199	Further information 7.1: Classical mechanics	280
Discussion questions	200	Discussion questions	283
Exercises	201	Exercises	283
Problems	204	Problems	284

<b>Mathematical background 3: Complex numbers</b>	<b>286</b>	Further information 9.2: The energy of spin-orbit interaction	363
<b>MB3.1</b> Definitions	286	Discussion questions	363
<b>MB3.2</b> Polar representation	286	Exercises	364
<b>MB3.3</b> Operations	287	Problems	365
<b>8 Quantum theory: techniques and applications</b>	<b>288</b>	<b>Mathematical background 5: Vectors</b>	<b>368</b>
<b>Translational motion</b>	<b>288</b>	<b>MB5.1</b> Addition and subtraction	368
<b>8.1</b> A particle in a box	289	<b>MB5.2</b> Multiplication	369
<b>8.2</b> Motion in two and more dimensions	293	<b>MB5.3</b> Differentiation	369
<b>18.1</b> Impact on nanoscience: Quantum dots	295	<b>10 Molecular structure</b>	<b>371</b>
<b>8.3</b> Tunnelling	297	<b>The Born–Oppenheimer approximation</b>	<b>372</b>
<b>18.2</b> Impact on nanoscience: Scanning probe microscopy	299	<b>Valence-bond theory</b>	<b>372</b>
<b>Vibrational motion</b>	<b>300</b>	<b>10.1</b> Homonuclear diatomic molecules	372
<b>8.4</b> The energy levels	301	<b>10.2</b> Polyatomic molecules	374
<b>8.5</b> The wavefunctions	302	<b>Molecular orbital theory</b>	<b>378</b>
<b>Rotational motion</b>	<b>306</b>	<b>10.3</b> The hydrogen molecule-ion	378
<b>8.6</b> Rotation in two dimensions: a particle on a ring	306	<b>10.4</b> Homonuclear diatomic molecules	382
<b>8.7</b> Rotation in three dimensions: the particle on a sphere	310	<b>10.5</b> Heteronuclear diatomic molecules	388
<b>8.8</b> Spin	315	<b>110.1</b> Impact on biochemistry: The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	394
Checklist of key equations	317	<b>Molecular orbitals for polyatomic systems</b>	<b>395</b>
Discussion questions	317	<b>10.6</b> The Hückel approximation	395
Exercises	317	<b>10.7</b> Computational chemistry	401
Problems	319	<b>10.8</b> The prediction of molecular properties	405
<b>Mathematical background 4: Differential equations</b>	<b>322</b>	Checklist of key equations	407
<b>MB4.1</b> The structure of differential equations	322	Further information 10.1: Details of the Hartree–Fock method	408
<b>MB4.2</b> The solution of ordinary differential equations	322	Discussion questions	409
<b>MB4.3</b> The solution of partial differential equations	323	Exercises	409
<b>9 Atomic structure and spectra</b>	<b>324</b>	Problems	410
<b>The structure and spectra of hydrogenic atoms</b>	<b>324</b>	<b>Mathematical background 6: Matrices</b>	<b>414</b>
<b>9.1</b> The structure of hydrogenic atoms	325	<b>MB6.1</b> Definitions	414
<b>9.2</b> Atomic orbitals and their energies	330	<b>MB6.2</b> Matrix addition and multiplication	414
<b>9.3</b> Spectroscopic transitions and selection rules	339	<b>MB6.3</b> Eigenvalue equations	415
<b>The structures of many-electron atoms</b>	<b>340</b>	<b>11 Molecular symmetry</b>	<b>417</b>
<b>9.4</b> The orbital approximation	341	<b>The symmetry elements of objects</b>	<b>417</b>
<b>9.5</b> Self-consistent field orbitals	349	<b>11.1</b> Operations and symmetry elements	418
<b>The spectra of complex atoms</b>	<b>350</b>	<b>11.2</b> The symmetry classification of molecules	420
<b>9.6</b> Linewidths	350	<b>11.3</b> Some immediate consequences of symmetry	425
<b>9.7</b> Quantum defects and ionization limits	352	<b>Applications to molecular orbital theory and spectroscopy</b>	<b>427</b>
<b>9.8</b> Singlet and triplet states	353	<b>11.4</b> Character tables and symmetry labels	427
<b>9.9</b> Spin-orbit coupling	354	<b>11.5</b> Vanishing integrals and orbital overlap	433
<b>9.10</b> Term symbols and selection rules	357	<b>11.6</b> Vanishing integrals and selection rules	439
<b>19.1</b> Impact on astrophysics: Spectroscopy of stars	361		
Checklist of key equations	362		
Further information 9.1: The separation of motion	362		

Checklist of key equations	441	<b>The fates of electronically excited states</b>	<b>503</b>
Discussion questions	441	<b>13.4</b> Fluorescence and phosphorescence	503
Exercises	441	<b>I13.2</b> Impact on biochemistry: Fluorescence microscopy	507
Problems	442	<b>13.5</b> Dissociation and predissociation	507
		<b>13.6</b> Laser action	508
		Checklist of key equations	512
		Further information 13.1: Examples of practical lasers	513
		Discussion questions	515
		Exercises	515
		Problems	517
<b>12 Molecular spectroscopy 1: rotational and vibrational spectra</b>	<b>445</b>	<b>14 Molecular spectroscopy 3: magnetic resonance</b>	<b>520</b>
<b>General features of molecular spectroscopy</b>	<b>446</b>	<b>The effect of magnetic fields on electrons and nuclei</b>	<b>520</b>
<b>12.1</b> Experimental techniques	446	<b>14.1</b> The energies of electrons in magnetic fields	521
<b>12.2</b> Selection rules and transition moments	447	<b>14.2</b> The energies of nuclei in magnetic fields	522
<b>I12.1</b> Impact on astrophysics: Rotational and vibrational spectroscopy of interstellar species	447	<b>14.3</b> Magnetic resonance spectroscopy	523
<b>Pure rotation spectra</b>	<b>449</b>	<b>Nuclear magnetic resonance</b>	<b>524</b>
<b>12.3</b> Moments of inertia	449	<b>14.4</b> The NMR spectrometer	525
<b>12.4</b> The rotational energy levels	452	<b>14.5</b> The chemical shift	526
<b>12.5</b> Rotational transitions	456	<b>14.6</b> The fine structure	532
<b>12.6</b> Rotational Raman spectra	459	<b>14.7</b> Conformational conversion and exchange processes	539
<b>12.7</b> Nuclear statistics and rotational states	460	<b>Pulse techniques in NMR</b>	<b>540</b>
<b>The vibrations of diatomic molecules</b>	<b>462</b>	<b>14.8</b> The magnetization vector	540
<b>12.8</b> Molecular vibrations	462	<b>14.9</b> Spin relaxation	542
<b>12.9</b> Selection rules	464	<b>I14.1</b> Impact on medicine: Magnetic resonance imaging	546
<b>12.10</b> Anharmonicity	465	<b>14.10</b> Spin decoupling	548
<b>12.11</b> Vibration–rotation spectra	468	<b>14.11</b> The nuclear Overhauser effect	548
<b>12.12</b> Vibrational Raman spectra of diatomic molecules	469	<b>14.12</b> Two-dimensional NMR	550
<b>The vibrations of polyatomic molecules</b>	<b>470</b>	<b>14.13</b> Solid-state NMR	551
<b>12.13</b> Normal modes	471	<b>Electron paramagnetic resonance</b>	<b>553</b>
<b>12.14</b> Infrared absorption spectra of polyatomic molecules	472	<b>14.14</b> The EPR spectrometer	553
<b>I12.2</b> Impact on environmental science: Climate change	473	<b>14.15</b> The <i>g</i> -value	553
<b>12.15</b> Vibrational Raman spectra of polyatomic molecules	475	<b>14.16</b> Hyperfine structure	555
<b>12.16</b> Symmetry aspects of molecular vibrations	476	<b>I14.2</b> Impact on biochemistry and nanoscience: Spin probes	557
Checklist of key equations	479	Checklist of key equations	559
Further information 12.1: Spectrometers	479	Further information 14.1: Fourier transformation of the FID curve	559
Further information 12.2: Selection rules for rotational and vibrational spectroscopy	482	Discussion questions	559
Discussion questions	484	Exercises	560
Exercises	484	Problems	561
Problems	486	<b>15 Statistical thermodynamics 1: the concepts</b>	<b>564</b>
<b>13 Molecular spectroscopy 2: electronic transitions</b>	<b>489</b>	<b>The distribution of molecular states</b>	<b>565</b>
<b>The characteristics of electronic transitions</b>	<b>489</b>	<b>15.1</b> Configurations and weights	565
<b>13.1</b> Measurements of intensity	490	<b>15.2</b> The molecular partition function	568
<b>13.2</b> The electronic spectra of diatomic molecules	491		
<b>13.3</b> The electronic spectra of polyatomic molecules	498		
<b>I13.1</b> Impact on biochemistry: Vision	501		

<b>The internal energy and the entropy</b>	<b>574</b>	<b>17.6</b> Repulsive and total interactions	642
<b>15.3</b> The internal energy	574	<b>117.2</b> Impact on materials science: Hydrogen storage in molecular clathrates	643
<b>15.4</b> The statistical entropy	576		
<b>115.1</b> Impact on technology: Reaching very low temperatures	578	<b>Gases and liquids</b>	<b>643</b>
		<b>17.7</b> Molecular interactions in gases	644
<b>The canonical partition function</b>	<b>579</b>	<b>17.8</b> The liquid–vapour interface	645
<b>15.5</b> The canonical ensemble	579	<b>17.9</b> Surface films	649
<b>15.6</b> The thermodynamic information in the partition function	581	<b>17.10</b> Condensation	652
<b>15.7</b> Independent molecules	582	Checklist of key equations	653
Checklist of key equations	585	Further information 17.1: The dipole–dipole interaction	654
Further information 15.1: The Boltzmann distribution	585	Further information 17.2: The basic principles of molecular beams	654
Further information 15.2: The Boltzmann formula	587	Discussion questions	655
Discussion questions	588	Exercises	655
Exercises	588	Problems	656
Problems	590		
<b>16 Statistical thermodynamics 2: applications</b>	<b>592</b>	<b>18 Materials 1: macromolecules and self-assembly</b>	<b>659</b>
<b>Fundamental relations</b>	<b>592</b>	<b>Structure and dynamics</b>	<b>659</b>
<b>16.1</b> The thermodynamic functions	592	<b>18.1</b> The different levels of structure	660
<b>16.2</b> The molecular partition function	594	<b>18.2</b> Random coils	660
		<b>18.3</b> The mechanical properties of polymers	665
<b>Using statistical thermodynamics</b>	<b>601</b>	<b>18.4</b> The electrical properties of polymers	667
<b>16.3</b> Mean energies	601	<b>18.5</b> The structures of biological macromolecules	667
<b>16.4</b> Heat capacities	602		
<b>16.5</b> Equations of state	605	<b>Aggregation and self-assembly</b>	<b>671</b>
<b>16.6</b> Molecular interactions in liquids	607	<b>18.6</b> Colloids	671
<b>16.7</b> Residual entropies	609	<b>18.7</b> Micelles and biological membranes	674
<b>16.8</b> Equilibrium constants	610		
<b>116.1</b> Impact on biochemistry: The helix–coil transition in polypeptides	615	<b>Determination of size and shape</b>	<b>677</b>
Checklist of key equations	616	<b>18.8</b> Mean molar masses	678
Further information 16.1: The rotational partition function of a symmetric rotor	617	<b>18.9</b> The techniques	680
Discussion questions	618	Checklist of key equations	688
Exercises	618	Further information 18.1: Random and nearly random coils	689
Problems	619	Discussion questions	690
		Exercises	690
		Problems	691
<b>17 Molecular interactions</b>	<b>622</b>	<b>19 Materials 2: solids</b>	<b>695</b>
<b>Electric properties of molecules</b>	<b>622</b>	<b>Crystallography</b>	<b>695</b>
<b>17.1</b> Electric dipole moments	622	<b>19.1</b> Lattices and unit cells	695
<b>17.2</b> Polarizabilities	625	<b>19.2</b> The identification of lattice planes	697
<b>17.3</b> Polarization	626	<b>19.3</b> The investigation of structure	699
<b>17.4</b> Relative permittivities	628	<b>19.4</b> Neutron and electron diffraction	708
		<b>19.5</b> Metallic solids	709
<b>Interactions between molecules</b>	<b>631</b>	<b>19.6</b> Ionic solids	711
<b>17.5</b> Interactions between dipoles	631	<b>19.7</b> Molecular solids and covalent networks	714
<b>117.1</b> Impact on medicine: Molecular recognition and drug design	640	<b>119.1</b> Impact on biochemistry: X-ray crystallography of biological macromolecules	715

<b>The properties of solids</b>	<b>717</b>	<b>21 The rates of chemical reactions</b>	<b>782</b>
19.8 Mechanical properties	717	<b>Empirical chemical kinetics</b>	<b>782</b>
19.9 Electrical properties	719	21.1 Experimental techniques	783
I19.2 Impact on nanoscience: Nanowires	723	21.2 The rates of reactions	786
19.10 Optical properties	724	21.3 Integrated rate laws	790
19.11 Magnetic properties	728	21.4 Reactions approaching equilibrium	796
19.12 Superconductors	731	21.5 The temperature dependence of reaction rates	799
Checklist of key equations	733	<b>Accounting for the rate laws</b>	<b>802</b>
Further information 19.1: Solid state lasers and light-emitting diodes	733	21.6 Elementary reactions	802
Discussion questions	734	21.7 Consecutive elementary reactions	803
Exercises	735	<b>Examples of reaction mechanisms</b>	<b>809</b>
Problems	737	21.8 Unimolecular reactions	809
<b>Mathematical background 7: Fourier series and Fourier transforms</b>	<b>740</b>	21.9 Polymerization kinetics	811
MB7.1 Fourier series	740	21.10 Photochemistry	815
MB7.2 Fourier transforms	741	I21.1 Impact on biochemistry: Harvesting of light during plant photosynthesis	822
MB7.3 The convolution theorem	742	Checklist of key equations	825
		Discussion questions	825
<b>PART 3 Change</b>	<b>743</b>	Exercises	826
		Problems	828
<b>20 Molecules in motion</b>	<b>745</b>	<b>22 Reaction dynamics</b>	<b>831</b>
<b>Molecular motion in gases</b>	<b>745</b>	<b>Reactive encounters</b>	<b>831</b>
20.1 The kinetic model of gases	746	22.1 Collision theory	832
I20.1 Impact on astrophysics: The Sun as a ball of perfect gas	752	22.2 Diffusion-controlled reactions	839
20.2 Collisions with walls and surfaces	753	22.3 The material balance equation	842
20.3 The rate of effusion	754	<b>Transition state theory</b>	<b>843</b>
20.4 Transport properties of a perfect gas	755	22.4 The Eyring equation	844
<b>Molecular motion in liquids</b>	<b>758</b>	22.5 Thermodynamic aspects	848
20.5 Experimental results	758	<b>The dynamics of molecular collisions</b>	<b>851</b>
20.6 The conductivities of electrolyte solutions	759	22.6 Reactive collisions	851
20.7 The mobilities of ions	760	22.7 Potential energy surfaces	852
I20.2 Impact on biochemistry: Ion channels	764	22.8 Some results from experiments and calculations	853
<b>Diffusion</b>	<b>766</b>	<b>The dynamics of electron transfer</b>	<b>856</b>
20.8 The thermodynamic view	766	22.9 Electron transfer in homogeneous systems	857
20.9 The diffusion equation	770	22.10 Electron transfer processes at electrodes	861
20.10 Diffusion probabilities	772	I22.1 Impact on technology: Fuel cells	867
20.11 The statistical view	773	Checklist of key equations	868
Checklist of key equations	774	Further information 22.1: The Gibbs energy of activation of electron transfer	868
Further information 20.1: The transport characteristics of a perfect gas	775	Further information 22.2: The Butler–Volmer equation	869
Discussion questions	776	Discussion questions	871
Exercises	777	Exercises	871
Problems	779	Problems	873

<b>23 Catalysis</b>	<b>876</b>	<b>I23.1</b> Impact on technology: Catalysis in the chemical industry	900
<b>Homogeneous catalysis</b>	<b>876</b>	Checklist of key equations	903
<b>23.1</b> Features of homogeneous catalysis	876	Further information 23.1: The BET isotherm	903
<b>23.2</b> Enzymes	878	Discussion questions	904
<b>Heterogeneous catalysis</b>	<b>884</b>	Exercises	904
<b>23.3</b> The growth and structure of solid surfaces	885	Problems	906
<b>23.4</b> The extent of adsorption	888		
<b>23.5</b> The rates of surface processes	894	Resource section	909
<b>23.6</b> Mechanisms of heterogeneous catalysis	897	Answers to exercises and problems	948
<b>23.7</b> Catalytic activity at surfaces	899	Index	959

# List of impact sections

---

## Impact on astrophysics

<b>I9.1</b>	Spectroscopy of stars	361
<b>I12.1</b>	Rotational and vibrational spectroscopy of interstellar species	447
<b>I20.1</b>	The Sun as a ball of perfect gas	752

## Impact on biochemistry

<b>I2.1</b>	Differential scanning calorimetry	62
<b>I6.1</b>	Energy conversion in biological cells	211
<b>I10.1</b>	The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	394
<b>I13.1</b>	Vision	501
<b>I13.2</b>	Fluorescence microscopy	507
<b>I14.2</b>	Spin probes	557
<b>I16.1</b>	The helix–coil transition in polypeptides	615
<b>I19.1</b>	X-ray crystallography of biological macromolecules	715
<b>I20.2</b>	Ion channels	764
<b>I21.1</b>	Harvesting of light during plant photosynthesis	822

## Impact on biology

<b>I2.2</b>	Food and energy reserves	70
<b>I5.1</b>	Osmosis in physiology and biochemistry	175
<b>I7.1</b>	Electron microscopy	259

## Impact on engineering

<b>I3.1</b>	Refrigeration	103
-------------	---------------	-----

## Impact on environmental science

<b>I1.1</b>	The gas laws and the weather	28
<b>I12.2</b>	Climate change	473

## Impact on materials science

<b>I3.2</b>	Crystal defects	112
<b>I5.2</b>	Liquid crystals	188
<b>I17.2</b>	Hydrogen storage in molecular clathrates	643



## Impact on medicine

<b>I14.1</b>	Magnetic resonance imaging	546
<b>I17.1</b>	Molecular recognition and drug design	640

## Impact on nanoscience

<b>I8.1</b>	Quantum dots	295
<b>I8.2</b>	Scanning probe microscopy	299
<b>I19.2</b>	Nanowires	723

## Impact on technology

<b>I4.1</b>	Supercritical fluids	142
<b>I6.2</b>	Supramolecular chemistry	226
<b>I6.3</b>	Species-selective electrodes	239
<b>I15.1</b>	Reaching very low temperatures	578
<b>I22.1</b>	Fuel cells	867
<b>I23.1</b>	Catalysis in the chemical industry	900