

The third edition of this book has been completely revised. It is intended for first- and second-year undergraduates in chemistry, and for undergraduates in other science and engineering subjects which require an understanding of chemistry.

The author gives more attention to the solid and liquid states than is found in most other books on physical chemistry, and introduces topics such as computer simulation and quasicrystals. Each chapter concludes with a set of problems designed to lead the reader to familiarity with the subject and its application in new situations. Computer programs designed to assist the reader are downloadable from the Worldwide Web (www.cup.cam.ac.uk). Detailed solutions to the problems are available on the same internet, while brief answers are contained within the book itself. Stereoviews are presented for three-dimensional structures and instructions for viewing them are provided. The book assumes only pre-degree mathematics, and special mathematical and other topics are contained in appendices.

This modern text on physical chemistry will be of interest to undergraduate students in chemistry and also to students in other areas of science and engineering requiring a familiarity with the subject.

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*To the memory of
Dr W H Lee*

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Introduction to physical chemistry

3rd Edition

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Department of Chemistry, University of Surrey



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CONTENTS

<i>Preface</i>	<i>page</i> xvi
<i>Physical constants and other numerical data</i>	xviii
1 Structure, energy, mechanism	1
1.1 Introduction	1
1.2 Structure	1
1.3 Energy	3
1.4 Mechanism	5
Problems 1	7
2 Atoms, molecules and their structures	9
2.1 Introduction	9
2.2 Classical mechanics	9
2.3 Conflict with experiment	10
2.3.1 Black-body radiation	10
2.3.2 Photoelectric effect	13
2.3.3 Compton effect	14
2.3.4 Diffraction of electrons	14
2.3.5 Atomic spectra of hydrogen	14
2.4 Wave-particle duality	15
2.5 Quantum mechanics of particles	16
2.5.1 Born's interpretation of the wave equation	17
2.5.2 Uncertainty principle	17
2.5.3 Normalization and quantization	19
2.5.4 Particle in a one-dimensional box: quantization of translational energy	20
2.5.4.1 Tunnelling	22
2.5.5 Boxes of higher dimensions	22
2.6 Vibrational and rotational motion	23
2.6.1 Vibrational motion	23
2.6.2 Rotational motion	24
2.6.3 Space and spin quantization	25
2.7 Structure of the hydrogen atom	26
2.7.1 Atomic orbitals	27
2.7.2 Orbital terminology	32
2.7.3 Selection rules for atoms	35
2.8 Atoms with more than one electron	35
2.8.1 Screening	36
2.9 <i>Aufbau</i> principle	36
2.10 Ionization energy	39
2.11 Structures of molecules	43

2.11.1	Variation method	44
2.11.2	Linear combination of atomic orbitals	46
2.11.3	Overlap integral	47
2.11.4	Coulomb integral	47
2.11.5	Orthogonality	48
2.11.6	Methods for molecules	48
2.11.7	Hydrogen-molecule ion	49
2.11.7.1	Bonding and antibonding orbitals	50
2.11.8	Pauli principle	51
2.11.9	Homonuclear diatomic molecules	53
2.11.10	Symmetry of orbitals	54
2.11.11	Heteronuclear diatomic molecules	56
2.11.12	Electronegativity	58
2.11.13	Hybridization	59
2.11.14	Polyatomic molecules	60
2.11.14.1	Water	60
2.11.14.2	Methane	64
2.11.14.3	Delocalized systems	64
2.12	Hückel molecular-orbital theory	66
2.12.1	Delocalization energy	68
2.12.2	π -Bond order	69
2.12.3	Free-valence index	70
2.12.4	Aromatic systems	70
2.12.5	Charge distribution	71
2.13	Valence-shell electron-pair repulsion theory	73
2.14	Ligand-field theory	75
2.14.1	Magnetic properties	77
2.15	Apparently abnormal valence	79
	Problems 2	79
3	Determination of structure	83
3.1	Introduction	83
3.2	Symmetry concepts	83
3.3	Symmetry elements and symmetry operations	85
3.3.1	Rotation	85
3.3.2	Reflection	86
3.3.3	Roto-reflection	87
3.3.4	Roto-inversion	87
3.3.5	Inversion	87
3.3.6	Identity	87
3.3.7	Symmetry and chirality	87
3.4	Group theory	88
3.4.1	Group postulates	88
3.4.2	Group multiplication tables	89
3.4.3	Similarity transformations	90
3.4.4	Representations	91
3.4.5	Degenerate representations	93
3.4.6	Some applications of group theory	95
3.4.6.1	Carbonate ion	95
3.4.6.2	Methane	97
3.4.6.3	LCAO approximations	98
3.4.6.4	Projection operators	100
3.4.6.5	Vanishing integrals	102

Contents

ix

3.5 Symmetry of crystals	104
3.5.1 Lattices and unit cells	104
3.5.1.1 Translation unit cells	107
3.5.2 Reciprocal lattice	108
3.5.3 Space groups	109
3.5.3.1 Space groups <i>P2₁/c</i> and <i>Imma</i>	110
3.6 Spectroscopic methods in structure determination	113
3.6.1 Experimental procedure in spectroscopy	113
3.6.1.1 Fourier-transform spectroscopy	115
3.6.1.2 Spectral intensities	115
3.6.2 Spectra of atoms	116
3.6.2.1 Ionization energy of atomic sodium	116
3.6.2.2 Electron affinities for the halogens	117
3.6.2.3 Zeeman effect	117
3.6.3 Spectra of molecules	119
3.6.4 Rotational spectra	120
3.6.4.1 Moments of inertia	120
3.6.4.2 Microwave spectra of linear molecules	120
3.6.4.3 Stark effect	121
3.6.5 Vibrational spectra	122
3.6.5.1 Anharmonic motion	122
3.6.5.2 Bond force-constants and dissociation energies	123
3.6.5.3 Vibrations of polyatomic molecules	124
3.6.6 Raman spectroscopy	125
3.6.7 Spectral activity and symmetry	125
3.6.7.1 Direct product	127
3.6.8 Infrared spectra in structure determination	128
3.6.8.1 Examination of an infrared spectrum	129
3.6.9 Nuclear magnetic resonance spectroscopy	132
3.6.9.1 Shielding and the chemical shift	134
3.6.9.2 Coupling	135
3.6.9.3 Examination of a NMR spectrum	137
3.6.9.4 Other NMR techniques	137
3.6.10 Mass spectrometry	138
3.6.10.1 Isotopic variation	139
3.6.10.2 Examination of a mass spectrogram	140
3.6.11 X-ray crystallographic analysis	140
3.6.11.1 Bragg equation	141
3.6.11.2 Ewald's reciprocal space construction	142
3.6.11.3 Recording an X-ray diffraction pattern	143
3.6.11.4 X-ray scattering by an atom and a unit cell	145
3.6.11.5 Features of the structure factor equation	148
3.6.11.6 Representation of electron density by a Fourier series	150
3.6.11.7 Patterson function	152
3.6.11.8 Solution of a crystal structure by the heavy-atom method	153
Problems 3	158
4 Energy and energetics	165
4.1 Introduction	165
4.1.1 General laws of thermodynamics	165
4.1.2 Systems, states, properties and processes	165
4.1.3 Energy, work and heat	166
4.2 Conservation of energy and the first law of thermodynamics	167

4.2.1	Extensive and intensive properties	168
4.2.2	Expansion of an ideal gas	168
4.2.3	Reversibility	169
4.3	State properties	173
4.4	Expansion under specified conditions	174
4.4.1	Constant volume processes	174
4.4.2	Constant pressure processes	174
4.4.3	Adiabatic expansion	175
4.5	Thermochemistry	176
4.5.1	Bond enthalpies	178
4.5.2	Variation of enthalpy change with temperature	180
4.5.3	Calorimetry	180
4.6	Second law of thermodynamics	181
4.6.1	Heat engines	184
4.6.1.1	Carnot cycle	184
4.6.1.2	Thermodynamic temperature scale	185
4.6.2	Entropy at the molecular level	185
4.6.3	Entropy calculations	187
4.6.4	Measurement of entropy and the third law of thermodynamics	187
4.6.4.1	Residual entropy	189
4.7	Helmholtz and Gibbs free energies	189
4.8	Maxwell's equations	191
4.8.1	Equations of state	192
4.9	Gibbs free energy and chemical potential	192
4.9.1	Gibbs free energy and the ideal gas	193
4.9.2	Chemical potential	193
4.9.3	Chemical potential and real gases	194
4.9.4	Thermodynamics of mixing	195
	Problems 4	196
5	States of matter: gases and liquids	199
5.1	Introduction	199
5.2	Gases	199
5.2.1	Combination of Boyle's and Charles' laws	199
5.2.2	Constant-volume gas thermometer	200
5.3	Ideality and the kinetic theory of gases	201
5.3.1	Pressure exerted by a gas	201
5.3.2	Equipartition	203
5.3.3	Gas laws from the kinetic theory	203
5.3.4	Maxwell–Boltzmann distribution of velocities	204
5.3.5	Maxwell–Boltzmann distribution of speeds	206
5.3.6	Deviations from ideality: real gases	208
5.3.7	Van der Waals' equation of state	209
5.3.8	Comparing gases	211
5.3.9	Intermolecular attraction	212
5.3.10	Molecular volume effect	212
5.3.11	Collision frequency	213
5.3.12	Mean free path	213
5.3.13	The Joule–Thomson effect	214
5.4	Intermolecular forces	216
5.4.1	Electric moments	216
5.4.2	Polarizability	216

Contents

xi

5.4.3 Ion–dipole interaction	217
5.4.4 Dipole–dipole interaction	218
5.4.5 Induced dipole–induced dipole interaction	219
5.5 Intermolecular potentials	221
5.6 Liquids	222
5.6.1 Liquid–gas equilibrium	222
5.6.2 Radial distribution function	226
5.6.2.1 Diffraction studies	226
5.6.3 Equation of state for a fluid	229
5.6.4 Monte Carlo method for liquid structure	230
5.6.5 Molecular dynamics method for liquid structure	232
5.6.6 Structure of liquid water	232
5.6.7 Use of physical models	234
Problems 5	237
6 States of matter: solids	239
6.1 Introduction	239
6.2 Amorphous solids	239
6.3 Molecular solids	240
6.3.1 Packing of molecules	243
6.3.2 Classification of solids	243
6.3.2.1 Noble gases	243
6.3.2.2 Nonmetallic elements	244
6.3.2.3 Small inorganic molecules	247
6.3.2.4 Organic compounds	248
6.3.2.5 Standard values for bond lengths and angles	249
6.3.2.6 Structural and physical characteristics of molecular compounds	250
6.4 Covalent solids	252
6.5 Metals	253
6.5.1 Metallic radii	255
6.5.2 Metallic bonding	255
6.5.3 Heat capacity	256
6.5.3.1 Einstein and Debye solids	256
6.5.3.2 Heat capacity paradox	258
6.5.4 Wave-mechanical free-electron theory	260
6.5.5 Band theory	261
6.5.6 Energy bands and molecular-orbital theory	264
6.5.6.1 Occupation of orbitals	265
6.5.7 Semiconductors and insulators	266
6.5.8 Structural and physical characteristics of metallic compounds	268
6.6 Bond type among elements	268
6.7 Ionic solids	269
6.8 Electrostatic model for lattice energy	269
6.8.1 Madelung constant	269
6.8.2 Lattice energy equation	270
6.9 Thermodynamic model for lattice energy	272
6.9.1 Precision of the thermodynamic lattice energy	274
6.10 Polarization in ionic compounds: precision of the electrostatic model for lattice energy	275
6.11 Approximate calculation of lattice energy	276
6.12 Uses of lattice energies	277
6.12.1 Electron affinities and thermodynamic parameters	277

6.12.2	Compound stability	277
6.12.3	Charge distribution on polyatomic ions	278
6.13	Crystal chemistry	281
6.13.1	Ionic radii	281
6.13.2	Radius ratio and AX structure types	284
6.13.3	Polarization in ionic structures	288
6.13.4	Radius ratio and AX_2 structure types	289
6.14	Structural and physical characteristics of ionic compounds	291
6.15	Vibrations and defects in ionic compounds	292
6.15.1	Absorption spectra	292
6.15.2	Heat capacity	293
6.15.3	Defects in crystals	294
6.15.3.1	Schottky defect	294
6.15.3.2	Frenkel defect	296
6.15.4	Defects and ion mobility	296
6.16	Quasicrystals	297
6.17	Liquid crystals	298
6.18	Molten salts	300
	Problems 6	301
7	Phase rule and properties of solutions	304
7.1	Introduction	304
7.2	Phase rule	304
7.3	Two-component systems	305
7.4	Thermodynamics of the phase rule	307
7.5	Thermodynamics of the p - T phase diagram	308
7.5.1	Liquid–vapour equilibrium	308
7.5.1.1	Vapour under applied pressure	309
7.6	Vapour pressure: Raoult's and Henry's laws	309
7.6.1	Nonideal solutions	311
7.6.2	Distillation	313
7.6.2.1	Lever rule	314
7.6.3	Maximum and minimum boiling-point systems	315
7.7	Partially miscible liquids	316
7.7.1	Steam-distillation	317
7.7.2	Solvent extraction	319
7.7.3	Distribution law	320
7.8	Elevation of the boiling-point	321
7.9	Depression of the freezing-point	322
7.10	Osmosis	326
7.11	Anomalous behaviour	329
7.12	Activities	330
7.12.1	Activity of a solvent	330
7.12.2	Activity of a solute	331
7.12.2.1	Partial molar volume: Gibbs–Duhem equation	332
7.12.2.2	Isopiestic method	334
7.13	Activity and molality	334
	Problems 7	335
8	Chemical equilibrium	338
8.1	Introduction	338
8.2	Mass action	338

Contents

xiii

8.3	Equilibrium and free energy	339
8.4	Temperature and pressure effects on equilibrium	342
8.5	Van 't Hoff equation	343
8.5.1	Heterogeneous equilibria	344
8.6	Solubility of ionic compounds	345
8.6.1	Standard states for solubility	346
8.6.1.1	Mean activity and activity coefficient	346
8.6.1.2	Standard state for solution	347
8.6.2	Solubility relationships	348
8.6.2.1	Two example calculations	348
8.6.3	Solubility and energy	349
8.6.4	Solubility product	352
8.6.4.1	Common ion effect and ionic strength	353
8.7	Acid–base equilibria	354
8.7.1	Strong acid–strong base equilibria	355
8.7.2	Weak/strong acid–strong/weak base equilibria	357
8.7.3	Weak acid–weak base equilibria	359
8.7.4	Buffer solutions	360
8.7.4.1	Van Slyke buffer index	361
8.7.5	Polyprotic acids	362
8.7.6	Acid–base indicators	364
8.7.7	Acid–base titrations	366
8.7.7.1	Titrations with strong acids and strong bases	366
8.7.7.2	Titrations involving weak acids or weak bases	366
8.7.7.3	Differential titration curves	367
8.7.8	Activities in acid–base equilibria	367
	Problems 8	368
9	Electrochemistry	371
9.1	Introduction	371
9.2	Electrical conduction	371
9.2.1	Laws of electrolysis	372
9.2.2	Electrical conductivity	372
9.2.2.1	Measurement of conductivity	373
9.2.3	Independent conductivities of ions	374
9.2.4	Dissociation of electrolytes	376
9.2.5	Transport properties	377
9.2.5.1	Ion mobilities	378
9.2.5.2	Transport numbers	379
9.2.5.3	Measurement of transport numbers	379
9.2.5.4	Conduction and hydration	381
9.2.6	Strong electrolytes	383
9.2.7	Ion association	384
9.2.8	Applications of conductivity measurements	386
9.2.8.1	Determination of solubility products	386
9.2.8.2	Determination of the charge on a complex ion	387
9.2.8.3	Acid–base titrations	387
9.3	Equilibrium electrochemistry	389
9.3.1	Measurement of EMF	391
9.3.2	Electrode (reduction) potentials	392
9.3.2.1	Subsidiary reference electrode	393
9.3.2.2	Liquid junction potential	395

9.3.3	Thermodynamics of galvanic cells	395
9.3.3.1	Measurement of standard reduction potentials	396
9.3.3.2	Measurement of activity coefficients	397
9.3.3.3	Variation of EMF with temperature	397
9.3.3.4	Measurement of partial molar entropies of ions	398
9.3.4	Concentration cells	398
9.3.5	Redox equilibria	400
9.3.6	Measurement of pH	400
9.3.6.1	Glass electrode	401
9.3.6.2	Specific-ion electrodes	401
9.3.7	Potentiometric titrations	402
9.3.7.1	Acid–base reactions	402
9.3.7.2	Precipitation reactions	404
9.3.7.3	Redox reactions	405
9.3.7.4	Electrochemical series	405
9.4	Nonequilibrium electrochemistry	406
9.4.1	Overpotential	406
9.4.2	Corrosion	407
9.4.2.1	Thermodynamics of corrosion	407
9.4.2.2	Corrosion inhibition	408
9.4.3	Fuel cells	408
	Problems 9	410
10	Chemical kinetics and mechanisms of chemical reactions	413
10.1	Introduction	413
10.2	Experimental methods in chemical kinetics	413
10.3	Rate and order of reaction	414
10.4	Integrated rate equations	415
10.4.1	First-order reactions	416
10.4.2	Second-order reactions	417
10.4.3	Half-life and order of reaction	419
10.5	Reactions tending to equilibrium	420
10.6	Consecutive reactions	422
10.7	Computer-simulation studies of kinetics	424
10.8	Reaction mechanism	426
10.8.1	Molecularity	426
10.8.2	Dependence of rates of simple reactions upon temperature	426
10.9	Unimolecular decay in first-order reactions	428
10.10	Chain reactions	430
10.10.1	Hydrogen–chlorine reaction	430
10.10.2	Hydrogen–bromine reaction	431
10.10.3	Hydrogen–iodine reaction	431
10.10.4	Thermal decomposition of ethanal	432
10.10.5	Hydrogen–oxygen reaction	432
10.11	Photochemical reactions	434
10.12	Catalysis	435
10.12.1	Homogeneous catalysis	435
10.12.1.1	Kinetic salt effects	436
10.12.2	Heterogeneous catalysis: adsorption	438
10.12.2.1	Langmuir adsorption isotherm	439
10.12.2.2	Other isotherms	440
10.12.2.3	Chemical reaction at a surface	440

<i>Contents</i>	xv
10.12.2.4 Enzyme catalysis	442
10.13 Third-order reactions	444
Problems 10	446
Appendix 1 Problem-solving with personal computers	450
Appendix 2 Stereoviewing	456
Appendix 3 Average classical thermal energies	457
Appendix 4 Reduced mass	459
Appendix 5 Spherical polar coordinates	461
Appendix 6 Gamma function	464
Appendix 7 Slater's rules	465
Appendix 8 Linear least squares and the propagation of errors	466
Appendix 9 Determinants and cofactors	469
Appendix 10 Solution of a second-order differential equation	471
Appendix 11 Separation of variables	472
Appendix 12 Overlap integrals	473
Appendix 13 Partial derivatives	474
Appendix 14 Numerical integration	476
Appendix 15 Fermi–Dirac statistics	479
Appendix 16 Calculation of Madelung constants	482
Appendix 17 The hypsometric formula: an example of the Boltzmann distribution	483
Appendix 18 Tables of physical data	485
<i>Bibliography</i>	492
<i>Answers to numerical problems</i>	495
<i>Index</i>	503

PREFACE

This book is a complete revision of an earlier work of the same title by the author and his late colleague, Dr W H Lee. It is intended to meet the requirements of students in their first and second years of a degree course in chemistry, or in those sciences for which chemistry forms a significant part, and so to prepare the ground for more advanced final-year studies in this subject.

The mathematical arguments that have been employed in the book should lie within the scope of any chemistry degree student, who will have studied mathematics to A-level, or its equivalent, at least. Physical chemistry is not a nonmathematical subject: any attempt to make it appear so will probably detract from the elegance that attends those approaches that have served this subject well. Some less familiar mathematical topics are discussed in appendices.

Each chapter has been provided with a set of problems designed to enhance the reader's appreciation of the subject matter and its application to new situations. A suggested scheme for solving problems has been given in Appendix 1. The ready availability of computers means that much more extensive data sets can be handled than would be reasonable with hand calculators.

To this end, a number of computer programs has been written, as outlined in Appendix 1. They have been made available on the Worldwide Web internet and may be accessed at web site www.cup.cam.ac.uk; the set of programs, with notes, may be obtained also from the author. The reader is encouraged to make full use of these facilities. The set of programs includes the derivation of point groups and practical point-group recognition, which have been used successfully by the author in teaching these subjects over many years, and the calculation of Madelung constants, in addition to other, more numerical procedures.

The detailed solutions to the problems are available on the same web site, while brief answers are provided within the book itself.

The SI system of units is used throughout the book. However, there are several instances, for example, wavenumber (cm^{-1}) or ionization energy (eV), for which current practice demands that these alternative units should, at least, appear. Competency in more than one system of units will enhance the reader's appreciation of the subject and its literature.

In the sections that discuss three-dimensional topics, such as Bravais lattices and crystal structures, many illustrations have been provided as stereoscopic views and directions for viewing them are given in Appendix 2. Sections on liquid structure, quasicrystals and Wigner–Seitz cells have been introduced, in order to broaden the scope of the treatment of the subject of physical chemistry.

The author is most appreciative of those publishers and authors who have given their permission to reproduce those illustrations that carry the appropriate acknowledgements. The author is very greatly indebted to colleagues who have assisted in the preparation of this

book: to Professor S F A Kettle, Professorial Fellow at the University of East Anglia, for reading the work in manuscript and for making a number of helpful suggestions; to Professor J R Jones, Head of the Department of Chemistry at the University of Surrey, for a careful reading of the book in proof, thereby eliminating some unforced errors; and finally to the publishers for their assistance and cooperation in bringing the work to a state of completion. Any infelicities that might remain are the sole responsibility of the author.

Mark Ladd

Note added at proof

The reader is cautioned to distinguish carefully between the italic ‘vee’ and the Greek *nu*. An example of their occurrence together is in equation (A3.5), p. 458, where the first of these characters is a ‘vee’.

PHYSICAL CONSTANTS AND OTHER NUMERICAL DATA

These data have been selected, or derived, from the compilation of E R Cohen and B N Taylor, *J. Phys. Chem. Ref. Data* (1988) **17**, 1795–1803; the values are reported in SI units. The figures in parentheses after each value represent the standard deviation to be applied to its last two digits; the values of c and ϵ_0 are *defined*. Although the data are presented here with their full precision, we shall rarely need to employ more than about the first four or five significant figures.

Speed of light in a vacuum	c	2.99792458	$\times 10^8$	m s^{-1}
Permittivity of a vacuum	ϵ_0	8.854187817	$\times 10^{-12}$	F m^{-1}
Permeability of a vacuum	μ_0	4π	$\times 10^{-7}$	H m^{-1}
Planck constant	h	6.6260755(40)	$\times 10^{-34}$	J Hz^{-1}
Elementary charge	e	1.60217733(49)	$\times 10^{-19}$	C
Avogadro constant	L	6.0221367(36)	$\times 10^{23}$	mol^{-1}
Atomic mass unit	u	1.6605402(10)	$\times 10^{-27}$	kg
Bohr magneton	μ_B	9.2740154(31)	$\times 10^{-24}$	J T
Rydberg constant	R_∞	1.0973731534(13)	$\times 10^7$	m^{-1}
Rydberg constant for hydrogen	R_H	1.0967758772(13)	$\times 10^7$	m^{-1}
Bohr radius	a_0	5.29177249(24)	$\times 10^{-11}$	m
Boltzmann constant	k_B	1.380658(12)	$\times 10^{-23}$	J K^{-1}
Molar gas constant	\mathcal{R}	8.314510(70)		$\text{J K}^{-1} \text{mol}^{-1}$
		0.0820577(7)		$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
Molar volume of ideal gas at 273.15 K and 101 325 Pa	V_m	22.41410(19)	$\times 10^{-3}$	$\text{m}^3 \text{mol}^{-1}$
Compton wavelength (electron)	λ_c	2.42631058(22)	$\times 10^{-12}$	m
Rest mass of electron	m_e	9.1093897(54)	$\times 10^{-31}$	kg
Rest mass of proton	m_p	1.6726231(10)	$\times 10^{-27}$	kg
Rest mass of neutron	m_n	1.6749286(10)	$\times 10^{-27}$	kg
Reduced mass of proton and electron pair	μ	9.1044313(54)	$\times 10^{-31}$	kg
Faraday	\mathcal{F}	9.6485309(29)	$\times 10^3$	C mol^{-1}
Ice-point temperature	T_{ice}	273.1500(01)		K

(Farad $\text{F} = \text{C V}^{-1}$; Tesla $\text{T} = 10^4 \text{ G}$ (gauss) = $\text{J C}^{-1} \text{m}^{-2} \text{s}$; Henry $\text{H} = \text{J C}^{-2} \text{s}^2$)

Some of the more important additional units are listed below.

Length

1 Å (ångström unit) = $10^{-10} \text{ m} = 10 \text{ nm}$

Energy

$$1 \text{ eV (electronvolt)} \equiv 1.60217733(49) \times 10^{-19} \text{ J}$$

$$1 \text{ cal (calorie)} = 4.184 \text{ J} \equiv 96.485309(29) \text{ kJ mol}^{-1}$$

$$1 \text{ cm}^{-1} \equiv 1.9864673(4) \times 10^{-23} \text{ J} \equiv 1.1962568(5) \times 10^{-2} \text{ kJ mol}^{-1}$$

Pressure

$$1 \text{ atm (atmosphere)} = 101\,325 \text{ Pa (N m}^{-2}\text{)} = 760 \text{ Torr} \equiv 760 \text{ mmHg}$$

Dipole moment

$$1 \text{ D (debye)} = 3.33564 \times 10^{-30} \text{ C m}$$

PREFIXES TO UNITS

The following prefixes to units are in common use.

femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
f	p	n	μ	m	c	d	k	M	G
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9