

term **dispersion** is a term carried over from this phenomenon to mean the variation of the refractive index, or of any property, with frequency.

### A3.10 Optical activity

The concept of refractive index is closely related to the property of optical activity. An **optically active** substance is a substance that rotates the plane of polarization of plane-polarized light. To understand this effect, it is useful to regard the incident plane-polarized beam as a superposition of two oppositely rotating circularly polarized components. By convention, in right-handed circularly polarized light the electric vector rotates clockwise as seen by an observer facing the oncoming beam (Fig. A3.8). On entering the medium, one component propagates faster than the other if their refractive indices are different. If the sample is of length  $l$ , the difference in the times of passage is

$$\Delta t = \frac{l}{c_L} - \frac{l}{c_R}$$

where  $c_R$  and  $c_L$  are the speeds of the two components in the medium. In terms of the refractive indices, the difference is

$$\Delta t = (n_R - n_L) \frac{l}{c}$$

The phase difference between the two components when they emerge from the sample is therefore

$$\Delta\theta = 2\pi v \Delta t = \frac{2\pi c \Delta t}{\lambda} = (n_R - n_L) \frac{2\pi l}{\lambda}$$

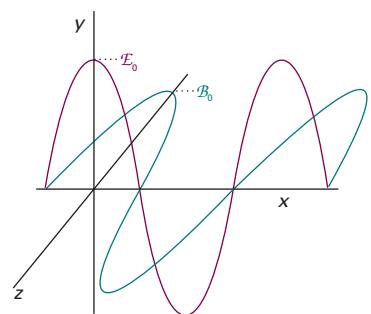
where  $\lambda$  is the wavelength of the light. The two rotating electric vectors have a different phase when they leave the sample from the value they had initially, so their superposition gives rise to a plane-polarized beam rotated through an angle  $\Delta\theta$  relative to the plane of the incoming beam. It follows that the angle of optical rotation is proportional to the difference in refractive index,  $n_R - n_L$ . A sample in which these two refractive indices are different is said to be **circularly birefringent**.

To explain why the refractive indices depend on the handedness of the light, we must examine why the polarizabilities depend on the handedness. One interpretation is that, if a molecule is helical (such as a polypeptide  $\alpha$ -helix described in Section 19.7) or a crystal has molecules in a helical arrangement (as in a cholesteric liquid crystal, as described in *Impact I6.1*), its polarizability depends on whether or not the electric field of the incident radiation rotates in the same sense as the helix.

Associated with the circular birefringence of the medium is a difference in absorption intensities for right- and left-circularly polarized radiation. This difference is known as *circular dichroism*, which is explored in Chapter 14.

## Electrostatics

**Electrostatics** is the study of the interactions of stationary electric charges. The elementary charge, the magnitude of charge carried by a single electron or proton, is  $e \approx 1.60 \times 10^{-19} \text{ C}$ . The magnitude of the charge per mole is Faraday's constant:  $F = N_A e = 9.65 \times 10^4 \text{ C mol}^{-1}$ .

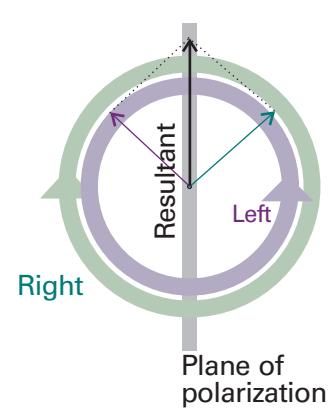


**Fig. A3.7** Electromagnetic radiation consists of a wave of electric and magnetic fields perpendicular to the direction of propagation (in this case the  $x$ -direction), and mutually perpendicular to each other. This illustration shows a plane-polarized wave, with the electric and magnetic fields oscillating in the  $xy$ - and  $xz$ -planes, respectively.

**Synoptic table A3.1\*** Refractive indices relative to air at 20°C

	434 nm	589 nm	656 nm
C <sub>6</sub> H <sub>6</sub> (l)	1.524	1.501	1.497
CS <sub>2</sub> (l)	1.675	1.628	1.618
H <sub>2</sub> O(l)	1.340	1.333	1.331
KI(s)	1.704	1.666	1.658

\* More values are given in the *Data section*.



**Fig. A3.8** The superposition of left and right circularly polarized light as viewed from an observer facing the oncoming beam.

### A3.11 The Coulomb interaction

If a point charge  $q_1$  is at a distance  $r$  in a vacuum from another point charge  $q_2$ , then their potential energy is

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r} \quad (\text{A3.30})$$

The constant  $\epsilon_0$  is the **vacuum permittivity**, a fundamental constant with the value  $8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ . This very important relation is called the **Coulomb potential energy** and the interaction it describes is called the **Coulomb interaction** of two charges. The Coulomb potential energy is equal to the work that must be done to bring up a charge  $q_1$  from infinity to a distance  $r$  from a charge  $q_2$ .

It follows from eqns A3.5 and A3.30 that the electrical force,  $F$ , exerted by a charge  $q_1$  on a second charge  $q_2$  has magnitude

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \quad (\text{A3.31})$$

The force itself is a vector directed along the line joining the two charges. With charge in coulombs and distance in metres, the force is obtained in newtons.

In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**,  $\epsilon$ , of the medium (see Section 18.3).

### A3.12 The Coulomb potential

The potential energy of a charge  $q_1$  in the presence of another charge  $q_2$  can be expressed in terms of the **Coulomb potential**,  $\phi$ :

$$V = q_1 \phi \quad \phi = \frac{q_2}{4\pi\epsilon_0 r} \quad (\text{A3.32})$$

The units of potential are joules per coulomb,  $\text{J C}^{-1}$ , so, when  $\phi$  is multiplied by a charge in coulombs, the result is in joules. The combination joules per coulomb occurs widely in electrostatics, and is called a *volt*, V:

$$1 \text{ V} = 1 \text{ J C}^{-1} \quad (\text{A3.33})$$

If there are several charges  $q_2, q_3, \dots$  present in the system, the total potential experienced by the charge  $q_1$  is the sum of the potential generated by each charge:

$$\phi = \phi_2 + \phi_3 + \dots \quad (\text{A3.34})$$

When the charge distribution is more complex than a single point-like object, the Coulomb potential is described in terms of a charge density,  $\rho$ . With charge in coulomb and length in metres, the charge density is expressed in coulombs per metre-cubed ( $\text{C m}^{-3}$ ). The electric potential arising from a charge distribution with density  $\rho$  is the solution to **Poisson's equation**:

$$\nabla^2 \phi = -\rho/\epsilon_0 \quad (\text{A3.35})$$

where  $\nabla^2 = (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ . If the distribution is spherically symmetrical, then so too is  $\phi$  and eqn A3.35 reduces to the form used in *Further information 5.1*.

### A3.13 The strength of the electric field

Just as the potential energy of a charge  $q_1$  can be written  $V = q_1 \phi$ , so the magnitude of the force on  $q_1$  can be written  $F = q_1 \mathcal{E}$ , where  $\mathcal{E}$  is the magnitude of the electric field

strength arising from  $q_2$  or from some more general charge distribution. The electric field strength (which, like the force, is actually a vector quantity) is the negative gradient of the electric potential:

$$\mathbf{E} = -\nabla\phi \quad (\text{A3.36})$$

### A3.14 Electric current and power

The motion of charge gives rise to an electric **current**,  $I$ . Electric current is measured in *ampere*, A, where

$$1 \text{ A} = 1 \text{ C s}^{-1} \quad (\text{A3.37})$$

If the current flows from a region of potential  $\phi_i$  to  $\phi_f$  through a **potential difference**  $\Delta\phi = \phi_f - \phi_i$ , the rate of doing work is the current (the rate of transfer of charge) multiplied by the potential difference,  $I\Delta\phi$ . The rate of doing electrical work is the **electrical power**,  $P$ , so

$$P = I\Delta\phi \quad (\text{A3.38})$$

With current in amperes and the potential difference in volts, the power works out in watts. The total energy,  $E$ , supplied in an interval  $\Delta t$  is the power (the rate of energy supply) multiplied by the duration of the interval:

$$E = P\Delta t = I\Delta\phi\Delta t \quad (\text{A3.39})$$

The energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds.

## Further reading

---

R.P. Feynman, R.B. Leighton, and M. Sands, *The Feynman lectures on physics*. Vols 1–3. Addison–Wesley, Reading (1966).

G.A.D. Ritchie and D.S. Sivia, *Foundations of physics for chemists*. Oxford Chemistry Primers, Oxford University Press (2000).

W.S. Warren, *The physical basis of chemistry*. Academic Press, San Diego (2000).

R. Wolfson and J.M. Pasachoff, *Physics for scientists and engineers*. Benjamin Cummings, San Francisco (1999).

# Data section

---

## Contents

The following is a directory of all tables in the text; those included in this *Data section* are marked with an asterisk. The remainder will be found on the pages indicated.

### Physical properties of selected materials\*

### Masses and natural abundances of selected nuclides\*

- 1.1 Pressure units (4)
- 1.2 The gas constant in various units (9)
- 1.3 The composition of dry air at sea level (11)
- 1.4 Second virial coefficients\*
- 1.5 Critical constants of gases\*
- 1.6 van der Waals coefficients\*
- 1.7 Selected equations of state (19)
  
- 2.1 Varieties of work (34)
- 2.2 Temperature variation of molar heat capacities\*
- 2.3 Standard enthalpies of fusion and vaporization at the transition temperature\*
- 2.4 Enthalpies of transition [notation] (51)
- 2.5 Thermodynamic data for organic compounds\*
- 2.6 Thermochemical properties of some fuels (53)
- 2.7 Thermodynamic data for inorganic compounds\*
- 2.7a Standard enthalpies of hydration at infinite dilution\*
- 2.7b Standard ion hydration enthalpies\*
- 2.8 Expansion coefficients and isothermal compressibilities\*
- 2.9 Inversion temperatures, normal freezing and boiling points, and Joule–Thomson coefficients\*
  
- 3.1 Standard entropies (and temperatures) of phase transitions\*
- 3.2 Standard entropies of vaporization of liquids\*
- 3.3 Standard Third-Law entropies [see Tables 2.5 and 2.7]\*
- 3.4 Standard Gibbs energies of formation [see Tables 2.5 and 2.7]\*
- 3.5 The Maxwell relations (104)
- 3.6 The fugacity of nitrogen\*
  
- 5.1 Henry's law constants for gases\*
- 5.2 Freezing point and boiling point constants\*
- 5.3 Standard states [summary of definitions] (158)
- 5.4 Ionic strength and molality (164)
- 5.5 Mean activity coefficients in water\*
- 5.6 Relative permitivities (dielectric constants)\*
  
- 7.1 Varieties of electrode (216)
- 7.2 Standard potentials\*
- 7.3 The electrochemical series of metals (\*)
- 7.4 Acidity constants for aqueous solutions\*
  
- 8.1 The Schrödinger equation (255)
- 8.2 Constraints of the uncertainty principle (271)
  
- 9.1 The Hermite polynomials (293)
- 9.2 The error function\*
- 9.3 The spherical harmonics (302)
- 9.4 Properties of angular momentum (309)
  
- 10.1 Hydrogenic radial wavefunctions (324)
- 10.2 Effective nuclear charge\*
- 10.3 Ionization energies\*
- 10.4 Electron affinities\*
  
- 11.1 Some hybridization schemes (368)
- 11.2 Bond lengths\*
- 11.3 Bond dissociation enthalpies\*
- 11.4 Pauling and Mulliken electronegativities\*
- 11.5 *Ab initio* calculations and spectroscopic data (398)
  
- 12.1 The notation for point groups (408)
- 12.2 The  $C_{2v}$  character table (415)
- 12.3 The  $C_{3v}$  character table (416)
  
- 13.1 Moments of inertia [formulae] (440)
- 13.2 Properties of diatomic molecules\*
- 13.3 Typical vibrational wavenumbers\*
  
- 14.1 Colour, frequency, and energy of light\*
- 14.2 Ground and excited states of  $O_2$  (483)
- 14.3 Absorption characteristics of some groups and molecules\*
- 14.4 Characteristics of laser radiation and their chemical applications (500)
  
- 15.1 Nuclear spin and nuclear structure (515)
- 15.2 Nuclear spin properties\*
- 15.3 Hyperfine coupling constants for atoms\*
  
- 17.1 Rotational and vibrational temperatures [see also Table 13.2] (594)

17.2	Symmetry numbers [see also Table 13.2] (596)	21.7	Debye–Hückel–Onsager coefficients for (1,1)-electrolytes*
17.3	Contributions to the molecular partition function [formulae] (615)	21.8	Diffusion coefficients*
17.4	Thermodynamic functions in terms of the partition function [formulae] (616)	22.1	Kinetic data for first-order reactions*
17.5	Contributions to mean energies and heat capacities [formulae] (616)	22.2	Kinetic data for second-order reactions*
18.1	Dipole moments, polarizabilities, and polarizability volumes*	22.3	Integrated rate laws (803)
18.2	Partial charges in polypeptides (622)	22.4	Arrhenius parameters*
18.3	Multipole interaction energies (630)	23.1	Photochemical processes (846)
18.4	Lennard-Jones (12,6)-potential parameters*	23.2	Common photophysical processes (846)
18.5	Surface tensions of liquids*	23.3	Values of $R_0$ for donor–acceptor pairs (852)
19.1	Radius of gyration*	24.1	Arrhenius parameters for gas-phase reactions*
19.2	Diffusion coefficients in water*	24.2	Arrhenius parameters for reactions in solution [see Table 22.4]*
19.3	Frictional coefficients and molecular geometry*	24.3	Summary of uses of $k$ [notation] (902)
19.4	Intrinsic viscosity*	25.1	Maximum observed enthalpies of physisorption*
20.1	The seven crystal systems (699)	25.2	Enthalpies of chemisorption*
20.2	The crystal structures of some elements (716)	25.3	Activation energies of catalysed reactions*
20.3	Ionic radii*	25.4	Properties of catalysts (929)
20.4	Madelung constants (719)	25.5	Chemisorption abilities (930)
20.5	Lattice enthalpies*	25.6	Exchange current densities and transfer coefficients*
20.6	Magnetic susceptibilities*	25.7	Summary of acronyms (950)
21.1	Collision cross-sections*	A1.1	The SI base units (960)
21.2	Transport properties of gases*	A1.2	A selection of derived units (961)
21.3	Transport properties of perfect gases [summary of formulae] (758)	A1.3	Common SI prefixes (961)
21.4	Viscosities of liquids*	A1.4	Some common units (962)
21.5	Limiting ionic conductivities in water*	A3.1	Refractive indices relative to air*
21.6	Ionic mobilities in water*		Character tables

The following tables reproduce and expand the data given in the short tables in the text, and follow their numbering. Standard states refer to a pressure of  $p^\circ = 1$  bar. The general references are as follows:

- AIP: D.E. Gray (ed.), *American Institute of Physics handbook*. McGraw Hill, New York (1972).
- AS: M. Abramowitz and I.A. Stegun (ed.), *Handbook of mathematical functions*. Dover, New York (1963).
- E: J. Emsley, *The elements*. Oxford University Press (1991).
- HCP: D.R. Lide (ed.), *Handbook of chemistry and physics*. CRC Press, Boca Raton (2000).
- JL: A.M. James and M.P. Lord, *Macmillan's chemical and physical data*. Macmillan, London (1992).
- KL: G.W.C. Kaye and T.H. Laby (ed.), *Tables of physical and chemical constants*. Longman, London (1973).
- LR: G.N. Lewis and M. Randall, revised by K.S. Pitzer and L. Brewer, *Thermodynamics*. McGraw-Hill, New York (1961).
- NBS: *NBS tables of chemical thermodynamic properties*, published as *J. Phys. and Chem. Reference Data*, 11, Supplement 2 (1982).
- RS: R.A. Robinson and R.H. Stokes, *Electrolyte solutions*. Butterworth, London (1959).
- TDOC: J.B. Pedley, J.D. Naylor, and S.P. Kirby, *Thermochemical data of organic compounds*. Chapman & Hall, London (1986).

## Physical properties of selected materials

	$\rho/\text{g cm}^{-3}$ at 293 K†	$T_f/\text{K}$	$T_b/\text{K}$		$\rho/\text{g cm}^{-3}$ at 293 K†	$T_f/\text{K}$	$T_b/\text{K}$	
<b>Elements</b>								
Aluminium(s)	2.698	933.5	2740	$\text{CaCO}_3(\text{s, calcite})$	2.71	1612	1171d	
Argon(g)	1.381	83.8	87.3	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$	2.284	383( $-\text{H}_2\text{O}$ )	423( $-5\text{H}_2\text{O}$ )	
Boron(s)	2.340	2573	3931	$\text{HBr}(\text{g})$	2.77	184.3	206.4	
Bromine(l)	3.123	265.9	331.9	$\text{HCl}(\text{g})$	1.187	159.0	191.1	
Carbon(s, gr)	2.260	3700s		$\text{HI}(\text{g})$	2.85	222.4	237.8	
Carbon(s, d)	3.513			$\text{H}_2\text{O}(\text{l})$	0.997	273.2	373.2	
Chlorine(g)	1.507	172.2	239.2	$\text{D}_2\text{O}(\text{l})$	1.104	277.0	374.6	
Copper(s)	8.960	1357	2840	$\text{NH}_3(\text{g})$	0.817	195.4	238.8	
Fluorine(g)	1.108	53.5	85.0	$\text{KBr}(\text{s})$	2.750	1003	1708	
Gold(s)	19.320	1338	3080	$\text{KCl}(\text{s})$	1.984	1049	1773s	
Helium(g)	0.125		4.22	$\text{NaCl}(\text{s})$	2.165	1074	1686	
Hydrogen(g)	0.071	14.0	20.3	$\text{H}_2\text{SO}_4(\text{l})$	1.841	283.5	611.2	
Iodine(s)	4.930	386.7	457.5	<b>Organic compounds</b>				
Iron(s)	7.874	1808	3023	Acetaldehyde, $\text{CH}_3\text{CHO}(\text{l, g})$	0.788	152	293	
Krypton(g)	2.413	116.6	120.8	Acetic acid, $\text{CH}_3\text{COOH}(\text{l})$	1.049	289.8	391	
Lead(s)	11.350	600.6	2013	Acetone, $(\text{CH}_3)_2\text{CO}(\text{l})$	0.787	178	329	
Lithium(s)	0.534	453.7	1620	Aniline, $\text{C}_6\text{H}_5\text{NH}_2(\text{l})$	1.026	267	457	
Magnesium(s)	1.738	922.0	1363	Anthracene, $\text{C}_{14}\text{H}_{10}(\text{s})$	1.243	490	615	
Mercury(l)	13.546	234.3	629.7	Benzene, $\text{C}_6\text{H}_6(\text{l})$	0.879	278.6	353.2	
Neon(g)	1.207	24.5	27.1	Carbon tetrachloride, $\text{CCl}_4(\text{l})$	1.63	250	349.9	
Nitrogen(g)	0.880	63.3	77.4	Chloroform, $\text{CHCl}_3(\text{l})$	1.499	209.6	334	
Oxygen(g)	1.140	54.8	90.2	Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$	0.789	156	351.4	
Phosphorus(s, wh)	1.820	317.3	553	Formaldehyde, $\text{HCHO}(\text{g})$		181	254.0	
Potassium(s)	0.862	336.8	1047	Glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	1.544	415		
Silver(s)	10.500	1235	2485	Methane, $\text{CH}_4(\text{g})$		90.6	111.6	
Sodium(s)	0.971	371.0	1156	Methanol, $\text{CH}_3\text{OH}(\text{l})$	0.791	179.2	337.6	
Sulfur(s, $\alpha$ )	2.070	386.0	717.8	Naphthalene, $\text{C}_{10}\text{H}_8(\text{s})$	1.145	353.4	491	
Uranium(s)	18.950	1406	4018	Octane, $\text{C}_8\text{H}_{18}(\text{l})$	0.703	216.4	398.8	
Xenon(g)	2.939	161.3	166.1	Phenol, $\text{C}_6\text{H}_5\text{OH}(\text{s})$	1.073	314.1	455.0	
Zinc(s)	7.133	692.7	1180	Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	1.588	457d		

d: decomposes; s: sublimes; Data: AIP, E, HCP, KL. † For gases, at their boiling points.

Masses and natural abundances of selected nuclides

Nuclide	<i>m/u</i>	Abundance/%
H <sup>1</sup> H	1.0078	99.985
	<sup>2</sup> H	2.0140 0.015
He <sup>3</sup> He	3.0160	0.000 13
	<sup>4</sup> He	4.0026 100
Li <sup>6</sup> Li	6.0151	7.42
	<sup>7</sup> Li	7.0160 92.58
B <sup>10</sup> B	10.0129	19.78
	<sup>11</sup> B	11.0093 80.22
C <sup>12</sup> C	12*	98.89
	<sup>13</sup> C	13.0034 1.11
N <sup>14</sup> N	14.0031	99.63
	<sup>15</sup> N	15.0001 0.37
O <sup>16</sup> O	15.9949	99.76
	<sup>17</sup> O	16.9991 0.037
	<sup>18</sup> O	17.9992 0.204
F <sup>19</sup> F	18.9984	100
P <sup>31</sup> P	30.9738	100
S <sup>32</sup> S	31.9721	95.0
	<sup>33</sup> S	32.9715 0.76
	<sup>34</sup> S	33.9679 4.22
Cl <sup>35</sup> Cl	34.9688	75.53
	<sup>37</sup> Cl	36.9651 24.4
Br <sup>79</sup> Br	78.9183	50.54
	<sup>81</sup> Br	80.9163 49.46
I <sup>127</sup> I	126.9045	100

\* Exact value.

**Table 1.4** Second virial coefficients,  $B/(cm^3 mol^{-1})$

	100 K	273 K	373 K	600 K
Air	-167.3	-13.5	3.4	19.0
Ar	-187.0	-21.7	-4.2	11.9
$CH_4$		-53.6	-21.2	8.1
$CO_2$		-142	-72.2	-12.4
$H_2$	-2.0	13.7	15.6	
He	11.4	12.0	11.3	10.4
Kr		-62.9	-28.7	1.7
$N_2$	-160.0	-10.5	6.2	21.7
Ne	-6.0	10.4	12.3	13.8
$O_2$	-197.5	-22.0	-3.7	12.9
Xe		-153.7	-81.7	-19.6

Data: AIP, JL. The values relate to the expansion in eqn 1.22 of Section 1.3b; convert to eqn 1.21 using  $B' = B/RT$ .

For Ar at 273 K,  $C = 1200 \text{ cm}^6 \text{ mol}^{-1}$ .

**Table 1.5** Critical constants of gases

	$p_c/\text{atm}$	$V_c/(cm^3 \text{ mol}^{-1})$	$T_c/\text{K}$	$Z_c$	$T_B/\text{K}$
Ar	48.00	75.25	150.72	0.292	411.5
$Br_2$	102	135	584	0.287	
$C_2H_4$	50.50	124	283.1	0.270	
$C_2H_6$	48.20	148	305.4	0.285	
$C_6H_6$	48.6	260	562.7	0.274	
$CH_4$	45.6	98.7	190.6	0.288	510.0
$Cl_2$	76.1	124	417.2	0.276	
$CO_2$	72.85	94.0	304.2	0.274	714.8
$F_2$	55	144			
$H_2$	12.8	64.99	33.23	0.305	110.0
$H_2O$	218.3	55.3	647.4	0.227	
HBr	84.0	363.0			
HCl	81.5	81.0	324.7	0.248	
He	2.26	57.76	5.21	0.305	22.64
HI	80.8	423.2			
Kr	54.27	92.24	209.39	0.291	575.0
$N_2$	33.54	90.10	126.3	0.292	327.2
Ne	26.86	41.74	44.44	0.307	122.1
$NH_3$	111.3	72.5	405.5	0.242	
$O_2$	50.14	78.0	154.8	0.308	405.9
Xe	58.0	118.8	289.75	0.290	768.0

Data: AIP, KL.

**Table 1.6** van der Waals coefficients

	$a/(atm\ dm^6\ mol^{-2})$	$b/(10^{-2}\ dm^3\ mol^{-1})$		$a/(atm\ dm^6\ mol^{-2})$	$b/(10^{-2}\ dm^3\ mol^{-1})$
Ar	1.337	3.20	H <sub>2</sub> S	4.484	4.34
C <sub>2</sub> H <sub>4</sub>	4.552	5.82	He	0.0341	2.38
C <sub>2</sub> H <sub>6</sub>	5.507	6.51	Kr	5.125	1.06
C <sub>6</sub> H <sub>6</sub>	18.57	11.93	N <sub>2</sub>	1.352	3.87
CH <sub>4</sub>	2.273	4.31	Ne	0.205	1.67
Cl <sub>2</sub>	6.260	5.42	NH <sub>3</sub>	4.169	3.71
CO	1.453	3.95	O <sub>2</sub>	1.364	3.19
CO <sub>2</sub>	3.610	4.29	SO <sub>2</sub>	6.775	5.68
H <sub>2</sub>	0.2420	2.65	Xe	4.137	5.16
H <sub>2</sub> O	5.464	3.05			

Data: HCP.

**Table 2.2** Temperature variation of molar heat capacities†

	$a$	$b/(10^{-3}\ K^{-1})$	$c/(10^5\ K^2)$
<b>Monatomic gases</b>			
	20.78	0	0
<b>Other gases</b>			
Br <sub>2</sub>	37.32	0.50	-1.26
Cl <sub>2</sub>	37.03	0.67	-2.85
CO <sub>2</sub>	44.22	8.79	-8.62
F <sub>2</sub>	34.56	2.51	-3.51
H <sub>2</sub>	27.28	3.26	0.50
I <sub>2</sub>	37.40	0.59	-0.71
N <sub>2</sub>	28.58	3.77	-0.50
NH <sub>3</sub>	29.75	25.1	-1.55
O <sub>2</sub>	29.96	4.18	-1.67
<b>Liquids (from melting to boiling)</b>			
C <sub>10</sub> H <sub>8</sub> , naphthalene	79.5	0.4075	0
I <sub>2</sub>	80.33	0	0
H <sub>2</sub> O	75.29	0	0
<b>Solids</b>			
Al	20.67	12.38	0
C (graphite)	16.86	4.77	-8.54
C <sub>10</sub> H <sub>8</sub> , naphthalene	-115.9	$3.920 \times 10^3$	0
Cu	22.64	6.28	0
I <sub>2</sub>	40.12	49.79	0
N <sub>2</sub> Cl	45.94	16.32	0
Pb	22.13	11.72	0.96

† For  $C_{p,m}/(J\ K^{-1}\ mol^{-1}) = a + bT + c/T^2$ .

Source: LR.

**Table 2.3** Standard enthalpies of fusion and vaporization at the transition temperature,  $\Delta_{\text{trs}}H^{\circ}/(\text{kJ mol}^{-1})$ 

	$T_f/\text{K}$	Fusion	$T_b/\text{K}$	Vaporization		$T_f/\text{K}$	Fusion	$T_b/\text{K}$	Vaporization
<b>Elements</b>									
Ag	1234	11.30	2436	250.6	$\text{CO}_2$	217.0	8.33	194.6	25.23 s
Ar	83.81	1.188	87.29	6.506	$\text{CS}_2$	161.2	4.39	319.4	26.74
$\text{Br}_2$	265.9	10.57	332.4	29.45	$\text{H}_2\text{O}$	273.15	6.008	373.15	40.656
$\text{Cl}_2$	172.1	6.41	239.1	20.41	$\text{H}_2\text{S}$	187.6	2.377	212.8	18.67
$\text{F}_2$	53.6	0.26	85.0	3.16	$\text{H}_2\text{SO}_4$	283.5	2.56		
$\text{H}_2$	13.96	0.117	20.38	0.916	$\text{NH}_3$	195.4	5.652	239.7	23.35
He	3.5	0.021	4.22	0.084	<b>Organic compounds</b>				
Hg	234.3	2.292	629.7	59.30	$\text{CH}_4$	90.68	0.941	111.7	8.18
$\text{I}_2$	386.8	15.52	458.4	41.80	$\text{CCl}_4$	250.3	2.5	350	30.0
$\text{N}_2$	63.15	0.719	77.35	5.586	$\text{C}_2\text{H}_6$	89.85	2.86	184.6	14.7
Na	371.0	2.601	1156	98.01	$\text{C}_6\text{H}_6$	278.61	10.59	353.2	30.8
$\text{O}_2$	54.36	0.444	90.18	6.820	$\text{C}_6\text{H}_{14}$	178	13.08	342.1	28.85
Xe	161	2.30	165	12.6	$\text{C}_{10}\text{H}_8$	354	18.80	490.9	51.51
K	336.4	2.35	1031	80.23	$\text{CH}_3\text{OH}$	175.2	3.16	337.2	35.27
<b>Inorganic compounds</b>									
$\text{CCl}_4$	250.3	2.47	349.9	30.00	$\text{C}_2\text{H}_5\text{OH}$	158.7	4.60	352	43.5

Data: AIP; s denotes sublimation.

**Table 2.5** Thermodynamic data for organic compounds (all values are for 298 K)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^{\circ}/(\text{kJ mol}^{-1})$	$\Delta_f G^{\circ}/(\text{kJ mol}^{-1})$	$S_m^{\circ}/(\text{J K}^{-1} \text{mol}^{-1})\dagger$	$C_{p,m}^{\circ}/(\text{J K}^{-1} \text{mol}^{-1})$	$\Delta_c H^{\circ}/(\text{kJ mol}^{-1})$
C(s) (graphite)	12.011	0	0	5.740	8.527	-393.51
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113	-395.40
$\text{CO}_2(\text{g})$	44.040	-393.51	-394.36	213.74	37.11	
<b>Hydrocarbons</b>						
$\text{CH}_4(\text{g})$ , methane	16.04	-74.81	-50.72	186.26	35.31	-890
$\text{CH}_3(\text{g})$ , methyl	15.04	+145.69	+147.92	194.2	38.70	
$\text{C}_2\text{H}_2(\text{g})$ , ethyne	26.04	+226.73	+209.20	200.94	43.93	-1300
$\text{C}_2\text{H}_4(\text{g})$ , ethene	28.05	+52.26	+68.15	219.56	43.56	-1411
$\text{C}_2\text{H}_6(\text{g})$ , ethane	30.07	-84.68	-32.82	229.60	52.63	-1560
$\text{C}_3\text{H}_6(\text{g})$ , propene	42.08	+20.42	+62.78	267.05	63.89	-2058
$\text{C}_3\text{H}_6(\text{g})$ , cyclopropane	42.08	+53.30	+104.45	237.55	55.94	-2091
$\text{C}_3\text{H}_8(\text{g})$ , propane	44.10	-103.85	-23.49	269.91	73.5	-2220
$\text{C}_4\text{H}_8(\text{g})$ , 1-butene	56.11	-0.13	+71.39	305.71	85.65	-2717
$\text{C}_4\text{H}_8(\text{g})$ , cis-2-butene	56.11	-6.99	+65.95	300.94	78.91	-2710
$\text{C}_4\text{H}_8(\text{g})$ , trans-2-butene	56.11	-11.17	+63.06	296.59	87.82	-2707
$\text{C}_4\text{H}_{10}(\text{g})$ , butane	58.13	-126.15	-17.03	310.23	97.45	-2878
$\text{C}_5\text{H}_{12}(\text{g})$ , pentane	72.15	-146.44	-8.20	348.40	120.2	-3537
$\text{C}_5\text{H}_{12}(\text{l})$	72.15	-173.1				
$\text{C}_6\text{H}_6(\text{l})$ , benzene	78.12	+49.0	+124.3	173.3	136.1	-3268

**Table 2.5** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_f H^\circ/(kJ\ mol^{-1})$	$\Delta_f G^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$	$\Delta_c H^\circ/(kJ\ mol^{-1})$
<b>Hydrocarbons (Continued)</b>						
$C_6H_6(g)$	78.12	+82.93	+129.72	269.31	81.67	-3302
$C_6H_{12}(l)$ , cyclohexane	84.16	-156	+26.8	204.4	156.5	-3920
$C_6H_{14}(l)$ , hexane	86.18	-198.7		204.3		-4163
$C_6H_5CH_3(g)$ , methylbenzene (toluene)	92.14	+50.0	+122.0	320.7	103.6	-3953
$C_7H_{16}(l)$ , heptane	100.21	-224.4	+1.0	328.6	224.3	
$C_8H_{18}(l)$ , octane	114.23	-249.9	+6.4	361.1		-5471
$C_8H_{18}(l)$ , iso-octane	114.23	-255.1				-5461
$C_{10}H_8(s)$ , naphthalene	128.18	+78.53				-5157
<b>Alcohols and phenols</b>						
$CH_3OH(l)$ , methanol	32.04	-238.66	-166.27	126.8	81.6	-726
$CH_3OH(g)$	32.04	-200.66	-161.96	239.81	43.89	-764
$C_2H_5OH(l)$ , ethanol	46.07	-277.69	-174.78	160.7	111.46	-1368
$C_2H_5OH(g)$	46.07	-235.10	-168.49	282.70	65.44	-1409
$C_6H_5OH(s)$ , phenol	94.12	-165.0	-50.9	146.0		-3054
<b>Carboxylic acids, hydroxy acids, and esters</b>						
$HCOOH(l)$ , formic	46.03	-424.72	-361.35	128.95	99.04	-255
$CH_3COOH(l)$ , acetic	60.05	-484.5	-389.9	159.8	124.3	-875
$CH_3COOH(aq)$	60.05	-485.76	-396.46	178.7		
$CH_3CO_2^-(aq)$	59.05	-486.01	-369.31	+86.6	-6.3	
$(COOH)_2(s)$ , oxalic	90.04	-827.2			117	-254
$C_6H_5COOH(s)$ , benzoic	122.13	-385.1	-245.3	167.6	146.8	-3227
$CH_3CH(OH)COOH(s)$ , lactic	90.08	-694.0				-1344
$CH_3COOC_2H_5(l)$ , ethyl acetate	88.11	-479.0	-332.7	259.4	170.1	-2231
<b>Alkanals and alkanones</b>						
$HCHO(g)$ , methanal	30.03	-108.57	-102.53	218.77	35.40	-571
$CH_3CHO(l)$ , ethanal	44.05	-192.30	-128.12	160.2		-1166
$CH_3CHO(g)$	44.05	-166.19	-128.86	250.3	57.3	-1192
$CH_3COCH_3(l)$ , propanone	58.08	-248.1	-155.4	200.4	124.7	-1790
<b>Sugars</b>						
$C_6H_{12}O_6(s)$ , $\alpha$ -D-glucose	180.16	-1274				-2808
$C_6H_{12}O_6(s)$ , $\beta$ -D-glucose	180.16	-1268	-910	212		
$C_6H_{12}O_6(s)$ , $\beta$ -D-fructose	180.16	-1266				-2810
$C_{12}H_{22}O_{11}(s)$ , sucrose	342.30	-2222	-1543	360.2		-5645
<b>Nitrogen compounds</b>						
$CO(NH_2)_2(s)$ , urea	60.06	-333.51	-197.33	104.60	93.14	-632
$CH_3NH_2(g)$ , methylamine	31.06	-22.97	+32.16	243.41	53.1	-1085
$C_6H_5NH_2(l)$ , aniline	93.13	+31.1				-3393
$CH_2(NH_2)COOH(s)$ , glycine	75.07	-532.9	-373.4	103.5	99.2	-969

Data: NBS, TDOC.  $\dagger$  Standard entropies of ions may be either positive or negative because the values are relative to the entropy of the hydrogen ion.

**Table 2.7** Thermodynamic data for elements and inorganic compounds (all values relate to 298 K)

	$M/(g\ mol^{-1})$	$\Delta_fH^\circ/(kJ\ mol^{-1})$	$\Delta_fG^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Aluminium (aluminum)</b>					
Al(s)	26.98	0	0	28.33	24.35
Al(l)	26.98	+10.56	+7.20	39.55	24.21
Al(g)	26.98	+326.4	+285.7	164.54	21.38
Al <sup>3+</sup> (g)	26.98	+5483.17			
Al <sup>3+</sup> (aq)	26.98	-531	-485	-321.7	
Al <sub>2</sub> O <sub>3</sub> (s, $\alpha$ )	101.96	-1675.7	-1582.3	50.92	79.04
AlCl <sub>3</sub> (s)	133.24	-704.2	-628.8	110.67	91.84
<b>Argon</b>					
Ar(g)	39.95	0	0	154.84	20.786
<b>Antimony</b>					
Sb(s)	121.75	0	0	45.69	25.23
SbH <sub>3</sub> (g)	124.77	+145.11	+147.75	232.78	41.05
<b>Arsenic</b>					
As(s, $\alpha$ )	74.92	0	0	35.1	24.64
As(g)	74.92	+302.5	+261.0	174.21	20.79
As <sub>4</sub> (g)	299.69	+143.9	+92.4	314	
AsH <sub>3</sub> (g)	77.95	+66.44	+68.93	222.78	38.07
<b>Barium</b>					
Ba(s)	137.34	0	0	62.8	28.07
Ba(g)	137.34	+180	+146	170.24	20.79
Ba <sup>2+</sup> (aq)	137.34	-537.64	-560.77	+9.6	
BaO(s)	153.34	-553.5	-525.1	70.43	47.78
BaCl <sub>2</sub> (s)	208.25	-858.6	-810.4	123.68	75.14
<b>Beryllium</b>					
Be(s)	9.01	0	0	9.50	16.44
Be(g)	9.01	+324.3	+286.6	136.27	20.79
<b>Bismuth</b>					
Bi(s)	208.98	0	0	56.74	25.52
Bi(g)	208.98	+207.1	+168.2	187.00	20.79
<b>Bromine</b>					
Br <sub>2</sub> (l)	159.82	0	0	152.23	75.689
Br <sub>2</sub> (g)	159.82	+30.907	+3.110	245.46	36.02
Br(g)	79.91	+111.88	+82.396	175.02	20.786
Br <sup>-</sup> (g)	79.91	-219.07			
Br <sup>-</sup> (aq)	79.91	-121.55	-103.96	+82.4	-141.8
HBr(g)	90.92	-36.40	-53.45	198.70	29.142
<b>Cadmium</b>					
Cd(s, $\gamma$ )	112.40	0	0	51.76	25.98
Cd(g)	112.40	+112.01	+77.41	167.75	20.79
Cd <sup>2+</sup> (aq)	112.40	-75.90	-77.612	-73.2	

**Table 2.7** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_fH^\ominus/(kJ\ mol^{-1})$	$\Delta_fG^\ominus/(kJ\ mol^{-1})$	$S_m^\ominus/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\ominus/(J\ K^{-1}\ mol^{-1})$
<b>Cadmium (Continued)</b>					
CdO(s)	128.40	-258.2	-228.4	54.8	43.43
CdCO <sub>3</sub> (s)	172.41	-750.6	-669.4	92.5	
<b>Caesium (cesium)</b>					
Cs(s)	132.91	0	0	85.23	32.17
Cs(g)	132.91	+76.06	+49.12	175.60	20.79
Cs <sup>+</sup> (aq)	132.91	-258.28	-292.02	+133.05	-10.5
<b>Calcium</b>					
Ca(s)	40.08	0	0	41.42	25.31
Ca(g)	40.08	+178.2	+144.3	154.88	20.786
Ca <sup>2+</sup> (aq)	40.08	-542.83	-553.58	-53.1	
CaO(s)	56.08	-635.09	-604.03	39.75	42.80
CaCO <sub>3</sub> (s) (calcite)	100.09	-1206.9	-1128.8	92.9	81.88
CaCO <sub>3</sub> (s) (aragonite)	100.09	-1207.1	-1127.8	88.7	81.25
CaF <sub>2</sub> (s)	78.08	-1219.6	-1167.3	68.87	67.03
CaCl <sub>2</sub> (s)	110.99	-795.8	-748.1	104.6	72.59
CaBr <sub>2</sub> (s)	199.90	-682.8	-663.6	130	
<b>Carbon (for 'organic' compounds of carbon, see Table 2.5)</b>					
C(s) (graphite)	12.011	0	0	5.740	8.527
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113
C(g)	12.011	+716.68	+671.26	158.10	20.838
C <sub>2</sub> (g)	24.022	+831.90	+775.89	199.42	43.21
CO(g)	28.011	-110.53	-137.17	197.67	29.14
CO <sub>2</sub> (g)	44.010	-393.51	-394.36	213.74	37.11
CO <sub>2</sub> (aq)	44.010	-413.80	-385.98	117.6	
H <sub>2</sub> CO <sub>3</sub> (aq)	62.03	-699.65	-623.08	187.4	
HCO <sub>3</sub> <sup>-</sup> (aq)	61.02	-691.99	-586.77	+91.2	
CO <sub>3</sub> <sup>2-</sup> (aq)	60.01	-677.14	-527.81	-56.9	
CCl <sub>4</sub> (l)	153.82	-135.44	-65.21	216.40	131.75
CS <sub>2</sub> (l)	76.14	+89.70	+65.27	151.34	75.7
HCN(g)	27.03	+135.1	+124.7	201.78	35.86
HCN(l)	27.03	+108.87	+124.97	112.84	70.63
CN <sup>-</sup> (aq)	26.02	+150.6	+172.4	+94.1	
<b>Chlorine</b>					
Cl <sub>2</sub> (g)	70.91	0	0	223.07	33.91
Cl(g)	35.45	+121.68	+105.68	165.20	21.840
Cl <sup>-</sup> (g)	34.45	-233.13			
Cl <sup>-</sup> (aq)	35.45	-167.16	-131.23	+56.5	-136.4
HCl(g)	36.46	-92.31	-95.30	186.91	29.12
HCl(aq)	36.46	-167.16	-131.23	56.5	-136.4
<b>Chromium</b>					
Cr(s)	52.00	0	0	23.77	23.35
Cr(g)	52.00	+396.6	+351.8	174.50	20.79

**Table 2.7** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_fH^\circ/(kJ\ mol^{-1})$	$\Delta_fG^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Chromium (Continued)</b>					
$\text{CrO}_4^{2-}(\text{aq})$	115.99	-881.15	-727.75	+50.21	
$\text{Cr}_2\text{O}_7^{2-}(\text{aq})$	215.99	-1490.3	-1301.1	+261.9	
<b>Copper</b>					
$\text{Cu}(\text{s})$	63.54	0	0	33.150	24.44
$\text{Cu}(\text{g})$	63.54	+338.32	+298.58	166.38	20.79
$\text{Cu}^+(\text{aq})$	63.54	+71.67	+49.98	+40.6	
$\text{Cu}^{2+}(\text{aq})$	63.54	+64.77	+65.49	-99.6	
$\text{Cu}_2\text{O}(\text{s})$	143.08	-168.6	-146.0	93.14	63.64
$\text{CuO}(\text{s})$	79.54	-157.3	-129.7	42.63	42.30
$\text{CuSO}_4(\text{s})$	159.60	-771.36	-661.8	109	100.0
$\text{CuSO}_4 \cdot \text{H}_2\text{O}(\text{s})$	177.62	-1085.8	-918.11	146.0	134
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$	249.68	-2279.7	-1879.7	300.4	280
<b>Deuterium</b>					
$\text{D}_2(\text{g})$	4.028	0	0	144.96	29.20
$\text{HD}(\text{g})$	3.022	+0.318	-1.464	143.80	29.196
$\text{D}_2\text{O}(\text{g})$	20.028	-249.20	-234.54	198.34	34.27
$\text{D}_2\text{O}(\text{l})$	20.028	-294.60	-243.44	75.94	84.35
$\text{HDO}(\text{g})$	19.022	-245.30	-233.11	199.51	33.81
$\text{HDO}(\text{l})$	19.022	-289.89	-241.86	79.29	
<b>Fluorine</b>					
$\text{F}_2(\text{g})$	38.00	0	0	202.78	31.30
$\text{F}(\text{g})$	19.00	+78.99	+61.91	158.75	22.74
$\text{F}^-(\text{aq})$	19.00	-332.63	-278.79	-13.8	-106.7
$\text{HF}(\text{g})$	20.01	-271.1	-273.2	173.78	29.13
<b>Gold</b>					
$\text{Au}(\text{s})$	196.97	0	0	47.40	25.42
$\text{Au}(\text{g})$	196.97	+366.1	+326.3	180.50	20.79
<b>Helium</b>					
$\text{He}(\text{g})$	4.003	0	0	126.15	20.786
<b>Hydrogen (see also deuterium)</b>					
$\text{H}_2(\text{g})$	2.016	0	0	130.684	28.824
$\text{H}(\text{g})$	1.008	+217.97	+203.25	114.71	20.784
$\text{H}^+(\text{aq})$	1.008	0	0	0	0
$\text{H}^+(\text{g})$	1.008	+1536.20			
$\text{H}_2\text{O}(\text{s})$	18.015			37.99	
$\text{H}_2\text{O}(\text{l})$	18.015	-285.83	-237.13	69.91	75.291
$\text{H}_2\text{O}(\text{g})$	18.015	-241.82	-228.57	188.83	33.58
$\text{H}_2\text{O}_2(\text{l})$	34.015	-187.78	-120.35	109.6	89.1
<b>Iodine</b>					
$\text{I}_2(\text{s})$	253.81	0	0	116.135	54.44
$\text{I}_2(\text{g})$	253.81	+62.44	+19.33	260.69	36.90

**Table 2.7** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_f H^\circ/(kJ\ mol^{-1})$	$\Delta_f G^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Iodine (Continued)</b>					
I(g)	126.90	+106.84	+70.25	180.79	20.786
I <sup>-</sup> (aq)	126.90	-55.19	-51.57	+111.3	-142.3
HI(g)	127.91	+26.48	+1.70	206.59	29.158
<b>Iron</b>					
Fe(s)	55.85	0	0	27.28	25.10
Fe(g)	55.85	+416.3	+370.7	180.49	25.68
Fe <sup>2+</sup> (aq)	55.85	-89.1	-78.90	-137.7	
Fe <sup>3+</sup> (aq)	55.85	-48.5	-4.7	-315.9	
Fe <sub>3</sub> O <sub>4</sub> (s) (magnetite)	231.54	-1118.4	-1015.4	146.4	143.43
Fe <sub>2</sub> O <sub>3</sub> (s) (haematite)	159.69	-824.2	-742.2	87.40	103.85
FeS(s, $\alpha$ )	87.91	-100.0	-100.4	60.29	50.54
FeS <sub>2</sub> (s)	119.98	-178.2	-166.9	52.93	62.17
<b>Krypton</b>					
Kr(g)	83.80	0	0	164.08	20.786
<b>Lead</b>					
Pb(s)	207.19	0	0	64.81	26.44
Pb(g)	207.19	+195.0	+161.9	175.37	20.79
Pb <sup>2+</sup> (aq)	207.19	-1.7	-24.43	+10.5	
PbO(s, yellow)	223.19	-217.32	-187.89	68.70	45.77
PbO(s, red)	223.19	-218.99	-188.93	66.5	45.81
PbO <sub>2</sub> (s)	239.19	-277.4	-217.33	68.6	64.64
<b>Lithium</b>					
Li(s)	6.94	0	0	29.12	24.77
Li(g)	6.94	+159.37	+126.66	138.77	20.79
Li <sup>+</sup> (aq)	6.94	-278.49	-293.31	+13.4	68.6
<b>Magnesium</b>					
Mg(s)	24.31	0	0	32.68	24.89
Mg(g)	24.31	+147.70	+113.10	148.65	20.786
Mg <sup>2+</sup> (aq)	24.31	-466.85	-454.8	-138.1	
MgO(s)	40.31	-601.70	-569.43	26.94	37.15
MgCO <sub>3</sub> (s)	84.32	-1095.8	-1012.1	65.7	75.52
MgCl <sub>2</sub> (s)	95.22	-641.32	-591.79	89.62	71.38
<b>Mercury</b>					
Hg(l)	200.59	0	0	76.02	27.983
Hg(g)	200.59	+61.32	+31.82	174.96	20.786
Hg <sup>2+</sup> (aq)	200.59	+171.1	+164.40	-32.2	
Hg <sub>2</sub> <sup>2+</sup> (aq)	401.18	+172.4	+153.52	+84.5	
HgO(s)	216.59	-90.83	-58.54	70.29	44.06
Hg <sub>2</sub> Cl <sub>2</sub> (s)	472.09	-265.22	-210.75	192.5	102
HgCl <sub>2</sub> (s)	271.50	-224.3	-178.6	146.0	
HgS(s, black)	232.65	-53.6	-47.7	88.3	

**Table 2.7** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_fH^\circ/(kJ\ mol^{-1})$	$\Delta_fG^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Neon</b>					
Ne(g)	20.18	0	0	146.33	20.786
<b>Nitrogen</b>					
N <sub>2</sub> (g)	28.013	0	0	191.61	29.125
N(g)	14.007	+472.70	+455.56	153.30	20.786
NO(g)	30.01	+90.25	+86.55	210.76	29.844
N <sub>2</sub> O(g)	44.01	+82.05	+104.20	219.85	38.45
NO <sub>2</sub> (g)	46.01	+33.18	+51.31	240.06	37.20
N <sub>2</sub> O <sub>4</sub> (g)	92.1	+9.16	+97.89	304.29	77.28
N <sub>2</sub> O <sub>5</sub> (s)	108.01	-43.1	+113.9	178.2	143.1
N <sub>2</sub> O <sub>5</sub> (g)	108.01	+11.3	+115.1	355.7	84.5
HNO <sub>3</sub> (l)	63.01	-174.10	-80.71	155.60	109.87
HNO <sub>3</sub> (aq)	63.01	-207.36	-111.25	146.4	-86.6
NO <sub>3</sub> <sup>-</sup> (aq)	62.01	-205.0	-108.74	+146.4	-86.6
NH <sub>3</sub> (g)	17.03	-46.11	-16.45	192.45	35.06
NH <sub>3</sub> (aq)	17.03	-80.29	-26.50	111.3	
NH <sub>4</sub> <sup>+</sup> (aq)	18.04	-132.51	-79.31	+113.4	79.9
NH <sub>2</sub> OH(s)	33.03	-114.2			
HN <sub>3</sub> (l)	43.03	+264.0	+327.3	140.6	43.68
HN <sub>3</sub> (g)	43.03	+294.1	+328.1	238.97	98.87
N <sub>2</sub> H <sub>4</sub> (l)	32.05	+50.63	+149.43	121.21	139.3
NH <sub>4</sub> NO <sub>3</sub> (s)	80.04	-365.56	-183.87	151.08	84.1
NH <sub>4</sub> Cl(s)	53.49	-314.43	-202.87	94.6	
<b>Oxygen</b>					
O <sub>2</sub> (g)	31.999	0	0	205.138	29.355
O(g)	15.999	+249.17	+231.73	161.06	21.912
O <sub>3</sub> (g)	47.998	+142.7	+163.2	238.93	39.20
OH <sup>-</sup> (aq)	17.007	-229.99	-157.24	-10.75	-148.5
<b>Phosphorus</b>					
P(s, wh)	30.97	0	0	41.09	23.840
P(g)	30.97	+314.64	+278.25	163.19	20.786
P <sub>2</sub> (g)	61.95	+144.3	+103.7	218.13	32.05
P <sub>4</sub> (g)	123.90	+58.91	+24.44	279.98	67.15
PH <sub>3</sub> (g)	34.00	+5.4	+13.4	210.23	37.11
PCl <sub>3</sub> (g)	137.33	-287.0	-267.8	311.78	71.84
PCl <sub>3</sub> (l)	137.33	-319.7	-272.3	217.1	
PCl <sub>5</sub> (g)	208.24	-374.9	-305.0	364.6	112.8
PCl <sub>5</sub> (s)	208.24	-443.5			
H <sub>3</sub> PO <sub>3</sub> (s)	82.00	-964.4			
H <sub>3</sub> PO <sub>3</sub> (aq)	82.00	-964.8			
H <sub>3</sub> PO <sub>4</sub> (s)	94.97	-1279.0	-1119.1	110.50	106.06
H <sub>3</sub> PO <sub>4</sub> (l)	94.97	-1266.9			
H <sub>3</sub> PO <sub>4</sub> (aq)	94.97	-1277.4	-1018.7	-222	

**Table 2.7** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_f H^\circ/(kJ\ mol^{-1})$	$\Delta_f G^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Phosphorus (Continued)</b>					
$\text{PO}_4^{3-}(\text{aq})$	94.97	-1277.4	-1018.7	-221.8	
$\text{P}_4\text{O}_{10}(\text{s})$	283.89	-2984.0	-2697.0	228.86	211.71
$\text{P}_4\text{O}_6(\text{s})$	219.89	-1640.1			
<b>Potassium</b>					
$\text{K}(\text{s})$	39.10	0	0	64.18	29.58
$\text{K}(\text{g})$	39.10	+89.24	+60.59	160.336	20.786
$\text{K}^+(\text{g})$	39.10	+514.26			
$\text{K}^+(\text{aq})$	39.10	-252.38	-283.27	+102.5	21.8
$\text{KOH}(\text{s})$	56.11	-424.76	-379.08	78.9	64.9
$\text{KF}(\text{s})$	58.10	-576.27	-537.75	66.57	49.04
$\text{KCl}(\text{s})$	74.56	-436.75	-409.14	82.59	51.30
$\text{KBr}(\text{s})$	119.01	-393.80	-380.66	95.90	52.30
$\text{KI}(\text{s})$	166.01	-327.90	-324.89	106.32	52.93
<b>Silicon</b>					
$\text{Si}(\text{s})$	28.09	0	0	18.83	20.00
$\text{Si}(\text{g})$	28.09	+455.6	+411.3	167.97	22.25
$\text{SiO}_2(\text{s}, \alpha)$	60.09	-910.94	-856.64	41.84	44.43
<b>Silver</b>					
$\text{Ag}(\text{s})$	107.87	0	0	42.55	25.351
$\text{Ag}(\text{g})$	107.87	+284.55	+245.65	173.00	20.79
$\text{Ag}^+(\text{aq})$	107.87	+105.58	+77.11	+72.68	21.8
$\text{AgBr}(\text{s})$	187.78	-100.37	-96.90	107.1	52.38
$\text{AgCl}(\text{s})$	143.32	-127.07	-109.79	96.2	50.79
$\text{Ag}_2\text{O}(\text{s})$	231.74	-31.05	-11.20	121.3	65.86
$\text{AgNO}_3(\text{s})$	169.88	-129.39	-33.41	140.92	93.05
<b>Sodium</b>					
$\text{Na}(\text{s})$	22.99	0	0	51.21	28.24
$\text{Na}(\text{g})$	22.99	+107.32	+76.76	153.71	20.79
$\text{Na}^+(\text{aq})$	22.99	-240.12	-261.91	59.0	46.4
$\text{NaOH}(\text{s})$	40.00	-425.61	-379.49	64.46	59.54
$\text{NaCl}(\text{s})$	58.44	-411.15	-384.14	72.13	50.50
$\text{NaBr}(\text{s})$	102.90	-361.06	-348.98	86.82	51.38
$\text{NaI}(\text{s})$	149.89	-287.78	-286.06	98.53	52.09
<b>Sulfur</b>					
$\text{S}(\text{s}, \alpha) \text{ (rhombic)}$	32.06	0	0	31.80	22.64
$\text{S}(\text{s}, \beta) \text{ (monoclinic)}$	32.06	+0.33	+0.1	32.6	23.6
$\text{S}(\text{g})$	32.06	+278.81	+238.25	167.82	23.673
$\text{S}_2(\text{g})$	64.13	+128.37	+79.30	228.18	32.47
$\text{S}^{2-}(\text{aq})$	32.06	+33.1	+85.8	-14.6	
$\text{SO}_2(\text{g})$	64.06	-296.83	-300.19	248.22	39.87
$\text{SO}_3(\text{g})$	80.06	-395.72	-371.06	256.76	50.67

**Table 2.7** (Continued)

	$M/(g\ mol^{-1})$	$\Delta_f H^\circ/(kJ\ mol^{-1})$	$\Delta_f G^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})^\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Sulfur (Continued)</b>					
H <sub>2</sub> SO <sub>4</sub> (l)	98.08	-813.99	-690.00	156.90	138.9
H <sub>2</sub> SO <sub>4</sub> (aq)	98.08	-909.27	-744.53	20.1	-293
SO <sub>4</sub> <sup>2-</sup> (aq)	96.06	-909.27	-744.53	+20.1	-293
HSO <sub>4</sub> <sup>-</sup> (aq)	97.07	-887.34	-755.91	+131.8	-84
H <sub>2</sub> S(g)	34.08	-20.63	-33.56	205.79	34.23
H <sub>2</sub> S(aq)	34.08	-39.7	-27.83	121	
HS <sup>-</sup> (aq)	33.072	-17.6	+12.08	+62.08	
SF <sub>6</sub> (g)	146.05	-1209	-1105.3	291.82	97.28
<b>Tin</b>					
Sn(s, $\beta$ )	118.69	0	0	51.55	26.99
Sn(g)	118.69	+302.1	+267.3	168.49	20.26
Sn <sup>2+</sup> (aq)	118.69	-8.8	-27.2	-17	
SnO(s)	134.69	-285.8	-256.9	56.5	44.31
SnO <sub>2</sub> (s)	150.69	-580.7	-519.6	52.3	52.59
<b>Xenon</b>					
Xe(g)	131.30	0	0	169.68	20.786
<b>Zinc</b>					
Zn(s)	65.37	0	0	41.63	25.40
Zn(g)	65.37	+130.73	+95.14	160.98	20.79
Zn <sup>2+</sup> (aq)	65.37	-153.89	-147.06	-112.1	46
ZnO(s)	81.37	-348.28	-318.30	43.64	40.25

Source: NBS.  $\dagger$  Standard entropies of ions may be either positive or negative because the values are relative to the entropy of the hydrogen ion.

**Table 2.7a** Standard enthalpies of hydration at infinite dilution,  $\Delta_{hyd}H^\circ/(kJ\ mol^{-1})$ 

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
F <sup>-</sup>	-1026	-911	-828	-806	-782
Cl <sup>-</sup>	-884	-783	-685	-664	-640
Br <sup>-</sup>	-856	-742	-658	-637	-613
I <sup>-</sup>	-815	-701	-617	-596	-572

Entries refer to X<sup>+</sup>(g) + Y<sup>-</sup>(g)  $\rightarrow$  X<sup>+</sup>(aq) + Y<sup>-</sup>(aq).

Data: Principally J.O'M. Bockris and A.K.N. Reddy, *Modern electrochemistry*, Vol. 1. Plenum Press, New York (1970).

**Table 2.7b** Standard ion hydration enthalpies,  $\Delta_{hyd}H^\circ/(kJ\ mol^{-1})$  at 298 K

Cations					
H <sup>+</sup>	(-1090)	Ag <sup>+</sup>	-464	Mg <sup>2+</sup>	-1920
Li <sup>+</sup>	-520	NH <sub>4</sub> <sup>+</sup>	-301	Ca <sup>2+</sup>	-1650
Na <sup>+</sup>	-405			Sr <sup>2+</sup>	-1480
K <sup>+</sup>	-321			Ba <sup>2+</sup>	-1360
Rb <sup>+</sup>	-300			Fe <sup>2+</sup>	-1950
Cs <sup>+</sup>	-277			Cu <sup>2+</sup>	-2100
				Zn <sup>2+</sup>	-2050
				Al <sup>3+</sup>	-4690
				Fe <sup>3+</sup>	-4430

**Anions**

OH <sup>-</sup>	-460
F <sup>-</sup>	-506

Entries refer to X<sup>±</sup>(g)  $\rightarrow$  X<sup>±</sup>(aq) based on H<sup>+</sup>(g)  $\rightarrow$  H<sup>+</sup>(aq);  $\Delta H^\circ = -1090\ kJ\ mol^{-1}$ . Data: Principally J.O'M. Bockris and A.K.N. Reddy, *Modern electrochemistry*, Vol. 1. Plenum Press, New York (1970).

**Table 2.8** Expansion coefficients,  $\alpha$ , and isothermal compressibilities,  $\kappa_T$ 

	$\alpha/(10^{-4} \text{ K}^{-1})$	$\kappa_T/(10^{-6} \text{ atm}^{-1})$
<b>Liquids</b>		
Benzene	12.4	92.1
Carbon tetrachloride	12.4	90.5
Ethanol	11.2	76.8
Mercury	1.82	38.7
Water	2.1	49.6
<b>Solids</b>		
Copper	0.501	0.735
Diamond	0.030	0.187
Iron	0.354	0.589
Lead	0.861	2.21

The values refer to 20°C.

Data: AIP( $\alpha$ ), KL( $\kappa_T$ ).**Table 2.9** Inversion temperatures, normal freezing and boiling points, and Joule–Thomson coefficients at 1 atm and 298 K

	$T_I/\text{K}$	$T_f/\text{K}$	$T_b/\text{K}$	$\mu_{JT}/(\text{K atm}^{-1})$
Air	603			0.189 at 50°C
Argon	723	83.8	87.3	
Carbon dioxide	1500	194.7s		1.11 at 300 K
Helium	40		4.22	-0.062
Hydrogen	202	14.0	20.3	-0.03
Krypton	1090	116.6	120.8	
Methane	968	90.6	111.6	
Neon	231	24.5	27.1	
Nitrogen	621	63.3	77.4	0.27
Oxygen	764	54.8	90.2	0.31

s: sublimes.

Data: AIP, JL, and M.W. Zemansky, *Heat and thermodynamics*. McGraw-Hill, New York (1957).**Table 3.1** Standard entropies (and temperatures) of phase transitions,  $\Delta_{trs}S^\circ/(J \text{ K}^{-1} \text{ mol}^{-1})$ 

	Fusion (at $T_f$ )	Vaporization (at $T_b$ )
Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Br <sub>2</sub>	39.76 (at 265.9 K)	88.61 (at 332.4 K)
C <sub>6</sub> H <sub>6</sub>	38.00 (at 278.6 K)	87.19 (at 353.2 K)
CH <sub>3</sub> COOH	40.4 (at 289.8 K)	61.9 (at 391.4 K)
CH <sub>3</sub> OH	18.03 (at 175.2 K)	104.6 (at 337.2 K)
Cl <sub>2</sub>	37.22 (at 172.1 K)	85.38 (at 239.0 K)
H <sub>2</sub>	8.38 (at 14.0 K)	44.96 (at 20.38 K)
H <sub>2</sub> O	22.00 (at 273.2 K)	109.0 (at 373.2 K)
H <sub>2</sub> S	12.67 (at 187.6 K)	87.75 (at 212.0 K)
He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22 K)
N <sub>2</sub>	11.39 (at 63.2 K)	75.22 (at 77.4 K)
NH <sub>3</sub>	28.93 (at 195.4 K)	97.41 (at 239.73 K)
O <sub>2</sub>	8.17 (at 54.4 K)	75.63 (at 90.2 K)

Data: AIP.

**Table 3.2** Standard entropies of vaporization of liquids at their normal boiling point

	$\Delta_{\text{vap}}H^\circ/\text{(kJ mol}^{-1}\text{)}$	$\theta_b/^\circ\text{C}$	$\Delta_{\text{vap}}S^\circ/\text{(J K}^{-1}\text{ mol}^{-1}\text{)}$
Benzene	30.8	80.1	+87.2
Carbon disulfide	26.74	46.25	+83.7
Carbon tetrachloride	30.00	76.7	+85.8
Cyclohexane	30.1	80.7	+85.1
Decane	38.75	174	+86.7
Dimethyl ether	21.51	-23	+86
Ethanol	38.6	78.3	+110.0
Hydrogen sulfide	18.7	-60.4	+87.9
Mercury	59.3	356.6	+94.2
Methane	8.18	-161.5	+73.2
Methanol	35.21	65.0	+104.1
Water	40.7	100.0	+109.1

Data: JL.

**Table 3.3** Standard Third-Law entropies at 298 K: see Tables 2.5 and 2.7**Table 3.4** Standard Gibbs energies of formation at 298 K: see Tables 2.5 and 2.7**Table 3.6** The fugacity coefficient of nitrogen at 273 K

$p/\text{atm}$	$\phi$	$p/\text{atm}$	$\phi$
1	0.999 55	300	1.0055
10	0.9956	400	1.062
50	0.9912	600	1.239
100	0.9703	800	1.495
150	0.9672	1000	1.839
200	0.9721		

Data: LR.

**Table 5.1** Henry's law constants for gases at 298 K,  $K/\text{(kPa kg mol}^{-1}\text{)}$ 

	Water	Benzene
$\text{CH}_4$	$7.55 \times 10^4$	$44.4 \times 10^3$
$\text{CO}_2$	$30.1 \times 10^3$	$8.90 \times 10^2$
$\text{H}_2$	$1.28 \times 10^5$	$2.79 \times 10^4$
$\text{N}_2$	$1.56 \times 10^5$	$1.87 \times 10^4$
$\text{O}_2$	$7.92 \times 10^4$	

Data: converted from R.J. Silbey and R.A. Alberty, *Physical chemistry*. Wiley, New York (2001).

**Table 5.2** Freezing-point and boiling-point constants

	$K_f/(K \text{ kg mol}^{-1})$	$K_b/(K \text{ kg mol}^{-1})$
Acetic acid	3.90	3.07
Benzene	5.12	2.53
Camphor	40	
Carbon disulfide	3.8	2.37
Carbon tetrachloride	30	4.95
Naphthalene	6.94	5.8
Phenol	7.27	3.04
Water	1.86	0.51

Data: KL.

**Table 5.5** Mean activity coefficients in water at 298 K

$b/b^\circ$	HCl	KCl	CaCl <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	LaCl <sub>3</sub>	In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
0.001	0.966	0.966	0.888	0.830	0.790	
0.005	0.929	0.927	0.789	0.639	0.636	0.16
0.01	0.905	0.902	0.732	0.544	0.560	0.11
0.05	0.830	0.816	0.584	0.340	0.388	0.035
0.10	0.798	0.770	0.524	0.266	0.356	0.025
0.50	0.769	0.652	0.510	0.155	0.303	0.014
1.00	0.811	0.607	0.725	0.131	0.387	
2.00	1.011	0.577	1.554	0.125	0.954	

Data: RS, HCP, and S. Glasstone, *Introduction to electrochemistry*. Van Nostrand (1942).**Table 5.6** Relative permittivities (dielectric constants) at 293 K

Nonpolar molecules	Polar molecules
Methane (at -173°C)	1.655
	Water
	78.54 (at 298 K)
	80.10
Carbon tetrachloride	2.238
	Ammonia
	16.9 (at 298 K)
	22.4 at -33°C
Cyclohexane	2.024
	Hydrogen sulfide
	9.26 at -85°C
	5.93 (at 283 K)
Benzene	2.283
	Methanol
	33.0
	Ethanol
	25.3
	Nitrobenzene
	35.6

Data: HCP.

**Table 7.2** Standard potentials at 298 K. (a) In electrochemical order

Reduction half-reaction	$E^\circ/V$	Reduction half-reaction	$E^\circ/V$
<b>Strongly oxidizing</b>			
$\text{H}_4\text{XeO}_6 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{XeO}_3 + 3\text{H}_2\text{O}$	+3.0	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.16
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07	$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	+0.07
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	+2.05	$\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	+1.98	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0, by definition
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.78	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Pb}^{4+} + 2\text{e}^- \rightarrow \text{Pb}^{2+}$	+1.67	$\text{In}^+ + \text{e}^- \rightarrow \text{In}$	-0.14
$2\text{HClO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.63	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	+1.61	$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	-0.15
$2\text{HBrO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$	+1.60	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	+1.51	$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$	-0.34
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.40	$\text{Ti}^+ + \text{e}^- \rightarrow \text{Ti}$	-0.34
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33	$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37
$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23	$\text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+$	-0.40
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.09	$\text{In}^{3+} + 2\text{e}^- \rightarrow \text{In}^+$	-0.44
$\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$	+0.97	$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.48
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96	$\text{In}^{3+} + \text{e}^- \rightarrow \text{In}^{2+}$	-0.49
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	+0.92	$\text{U}^{4+} + \text{e}^- \rightarrow \text{U}^{3+}$	-0.61
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.86	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	+0.80	$\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.79	$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.91
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}^- + 2\text{OH}^-$	+0.76	$\text{V}^{2+} + 2\text{e}^- \rightarrow \text{V}$	-1.19
$\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.62	$\text{Ti}^{2+} + 2\text{e}^- \rightarrow \text{Ti}$	-1.63
$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.60	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	+0.56	$\text{U}^{3+} + 3\text{e}^- \rightarrow \text{U}$	-1.79
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54	$\text{Sc}^{3+} + 3\text{e}^- \rightarrow \text{Sc}$	-2.09
$\text{CU}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.36
$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.53	$\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$	-2.48
$\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	+0.49	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.52
$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	+0.40	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36	$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}$	-2.89
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.91
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34	$\text{Ra}^{2+} + 2\text{e}^- \rightarrow \text{Ra}$	-2.92
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27	$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-2.92
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22	$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}$	-2.93
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$	+0.20	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
		$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05

**Table 7.2** Standard potentials at 298 K. (b) In electrochemical order

Reduction half-reaction	$E^\circ/V$	Reduction half-reaction	$E^\circ/V$
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	+1.98	$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.53
$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	+0.0713	$\text{In}^+ + \text{e}^- \rightarrow \text{In}$	-0.14
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22	$\text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+$	-0.40
$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45	$\text{In}^{3+} + 2\text{e}^- \rightarrow \text{In}^+$	-0.44
$\text{AgF} + \text{e}^- \rightarrow \text{Ag} + \text{F}^-$	+0.78	$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$	-0.34
$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	-0.15	$\text{In}^{3+} + \text{e}^- \rightarrow \text{In}^{2+}$	-0.49
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.52
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.40	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	+2.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.36
$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}$	-1.85	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$	+0.20	$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	+1.51
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.09	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}^- + 2\text{OH}^-$	+0.76	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87	$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	+0.56
$\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81	$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.60
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$	-2.48	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	+1.61	$\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	+0.49
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36	$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	-0.80
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$	+0.10
$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	+0.40
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$	-0.56
$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.91	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74	$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-2.92	$\text{Pb}^{4+} + 2\text{e}^- \rightarrow \text{Pb}^{2+}$	+1.67
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34	$\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}$	+1.20
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.16	$\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$	+0.97
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87	$\text{Ra}^{2+} + 2\text{e}^- \rightarrow \text{Ra}$	-2.92
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44	$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}$	-2.93
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04	$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.48
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	+2.05
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36	$\text{Sc}^{3+} + 3\text{e}^- \rightarrow \text{Sc}$	-2.09
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0, by definition	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$2\text{HBrO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$	+1.60	$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}$	-2.89
$2\text{HClO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.63	$\text{Ti}^{2+} + 2\text{e}^- \rightarrow \text{Ti}$	-1.63
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.78	$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37
$\text{H}_4\text{XeO}_6 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{XeO}_3 + 3\text{H}_2\text{O}$	+3.0	$\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.79	$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$	-0.34
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27	$\text{U}^{3+} + 3\text{e}^- \rightarrow \text{U}$	-1.79
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.86	$\text{U}^{4+} + \text{e}^- \rightarrow \text{U}^{3+}$	-0.61
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	+0.92	$\text{V}^{2+} + 2\text{e}^- \rightarrow \text{V}$	-1.19
$\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.62	$\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$	-0.26

**Table 7.4** Acidity constants for aqueous solutions at 298 K. (a) In order of acid strength

Acid	HA	A <sup>-</sup>	K <sub>a</sub>	pK <sub>a</sub>
Hydriodic	HI	I <sup>-</sup>	10 <sup>11</sup>	-11
Hydrobromic	HBr	Br <sup>-</sup>	10 <sup>9</sup>	-9
Hydrochloric	HCl	Cl <sup>-</sup>	10 <sup>7</sup>	-7
Sulfuric	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	10 <sup>2</sup>	-2
Perchloric*	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	4.0 × 10 <sup>1</sup>	-1.6
Hydronium ion	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	1	0.0
Oxalic	(COOH) <sub>2</sub>	HOOC CO <sub>2</sub> <sup>-</sup>	5.6 × 10 <sup>-2</sup>	1.25
Sulfurous	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	1.4 × 10 <sup>-2</sup>	1.85
Hydrogensulfate ion	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	1.0 × 10 <sup>-2</sup>	1.99
Phosphoric	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	6.9 × 10 <sup>-3</sup>	2.16
Glycinium ion	<sup>+</sup> NH <sub>3</sub> CH <sub>2</sub> COOH	NH <sub>2</sub> CH <sub>2</sub> COOH	4.5 × 10 <sup>-3</sup>	2.35
Hydrofluoric	HF	F <sup>-</sup>	6.3 × 10 <sup>-4</sup>	3.20
Formic	HCOOH	HCO <sub>2</sub> <sup>-</sup>	1.8 × 10 <sup>-4</sup>	3.75
Hydrogenoxalate ion	HOOCCO <sub>2</sub> <sup>-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1.5 × 10 <sup>-5</sup>	3.81
Lactic	CH <sub>3</sub> CH(OH)COOH	CH <sub>3</sub> CH(OH)CO <sub>2</sub> <sup>-</sup>	1.4 × 10 <sup>-4</sup>	3.86
Acetic (ethanoic)	CH <sub>3</sub> COOH	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	1.4 × 10 <sup>-5</sup>	4.76
Butanoic	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	1.5 × 10 <sup>-5</sup>	4.83
Propanoic	CH <sub>3</sub> CH <sub>2</sub> COOH	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	1.4 × 10 <sup>-5</sup>	4.87
Anilinium ion	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	1.3 × 10 <sup>-5</sup>	4.87
Pyridinium ion	C <sub>5</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> N	5.9 × 10 <sup>-6</sup>	5.23
Carbonic	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	4.5 × 10 <sup>-7</sup>	6.35
Hydrosulfuric	H <sub>2</sub> S	HS <sup>-</sup>	8.9 × 10 <sup>-8</sup>	7.05
Dihydrogenenphosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	6.2 × 10 <sup>-8</sup>	7.21
Hypochlorous	HClO	ClO <sup>-</sup>	4.0 × 10 <sup>-8</sup>	7.40
Hydrazinium ion	NH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> NH <sub>2</sub>	8 × 10 <sup>-9</sup>	8.1
Hypobromous	HBrO	BrO <sup>-</sup>	2.8 × 10 <sup>-9</sup>	8.55
Hydrocyanic	HCN	CN <sup>-</sup>	6.2 × 10 <sup>-10</sup>	9.21
Ammonium ion	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	5.6 × 10 <sup>-10</sup>	9.25
Boric*	B(OH) <sub>3</sub>	B(OH) <sub>4</sub> <sup>-</sup>	5.4 × 10 <sup>-10</sup>	9.27
Trimethylammonium ion	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	(CH <sub>3</sub> ) <sub>3</sub> N	1.6 × 10 <sup>-10</sup>	9.80
Phenol	C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	1.0 × 10 <sup>-10</sup>	9.99
Hydrogencarbonate ion	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	4.8 × 10 <sup>-11</sup>	10.33
Hypoiodous	HIO	IO <sup>-</sup>	3 × 10 <sup>-11</sup>	10.5
Ethylammonium ion	CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	2.2 × 10 <sup>-11</sup>	10.65
Methylammonium ion	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>2</sub>	2.2 × 10 <sup>-11</sup>	10.66
Dimethylammonium ion	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> NH	1.9 × 10 <sup>-11</sup>	10.73
Triethylammonium ion	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sup>+</sup>	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	1.8 × 10 <sup>-11</sup>	10.75
Diethylammonium ion	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH	1.4 × 10 <sup>-11</sup>	10.84
Hydrogenarsenate ion	HAsO <sub>4</sub> <sup>2-</sup>	AsO <sub>4</sub> <sup>3-</sup>	5.1 × 10 <sup>-12</sup>	11.29
Hydrogenphosphate ion	HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	4.8 × 10 <sup>-13</sup>	12.32
Hydrogensulfide ion	HS <sup>-</sup>	S <sup>2-</sup>	1.0 × 10 <sup>-19</sup>	19.00

\* At 293 K.

**Table 7.4** Acidity constants for aqueous solutions at 298 K. (b) In alphabetical order

Acid	HA	A <sup>-</sup>	K <sub>a</sub>	pK <sub>a</sub>
Acetic (ethanoic)	CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	1.4 × 10 <sup>-5</sup>	4.76
Ammonium ion	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	5.6 × 10 <sup>-10</sup>	9.25
Anilinium ion	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	1.3 × 10 <sup>-5</sup>	4.87
Boric*	B(OH) <sub>3</sub>	B(OH) <sub>4</sub> <sup>-</sup>	5.4 × 10 <sup>-10</sup>	9.27
Butanoic	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COO <sup>-</sup>	1.5 × 10 <sup>-5</sup>	4.83
Carbonic	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	4.5 × 10 <sup>-7</sup>	6.35
Diethylammonium ion	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH	1.4 × 10 <sup>-11</sup>	10.84
Dihydrogenphosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	6.2 × 10 <sup>-8</sup>	7.21
Dimethylammonium ion	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> NH	1.9 × 10 <sup>-11</sup>	10.73
Ethylammonium ion	CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	2.2 × 10 <sup>-11</sup>	10.65
Formic	HCOOH	HCO <sub>2</sub> <sup>-</sup>	1.8 × 10 <sup>-4</sup>	3.75
Glycinium ion	<sup>+</sup> NH <sub>3</sub> CH <sub>2</sub> COOH	NH <sub>2</sub> CH <sub>2</sub> COOH	4.5 × 10 <sup>-3</sup>	2.35
Hydrazinium ion	NH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> NH <sub>2</sub>	8 × 10 <sup>-9</sup>	8.1
Hydriodic	HI	I <sup>-</sup>	10 <sup>11</sup>	-11
Hydrobromic	HBr	Br <sup>-</sup>	10 <sup>9</sup>	-9
Hydrochloric	HCl	Cl <sup>-</sup>	10 <sup>7</sup>	-7
Hydrocyanic	HCN	CN <sup>-</sup>	6.2 × 10 <sup>-10</sup>	9.21
Hydrofluoric	HF	F <sup>-</sup>	6.3 × 10 <sup>-4</sup>	3.20
Hydrogenarsenate ion	HAsO <sub>4</sub> <sup>2-</sup>	AsO <sub>4</sub> <sup>3-</sup>	5.1 × 10 <sup>-12</sup>	11.29
Hydrogencarbonate ion	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	4.8 × 10 <sup>-11</sup>	10.33
Hydrogenoxalate ion	HOOC CO <sub>2</sub> <sup>-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1.5 × 10 <sup>-5</sup>	3.81
Hydrogenphosphate ion	HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	4.8 × 10 <sup>-13</sup>	12.32
Hydrogensulfate ion	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	1.0 × 10 <sup>-2</sup>	1.99
Hydrogensulfide ion	HS <sup>-</sup>	S <sup>2-</sup>	1.0 × 10 <sup>-19</sup>	19.00
Hydronium ion	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	1	0.0
Hydrosulfuric	H <sub>2</sub> S	HS <sup>-</sup>	8.9 × 10 <sup>-8</sup>	7.05
Hypobromous	HBrO	BrO <sup>-</sup>	2.8 × 10 <sup>-9</sup>	8.55
Hypoehlorous	HClO	ClO <sup>-</sup>	4.0 × 10 <sup>-8</sup>	7.40
Hypoiodous	HIO	IO <sup>-</sup>	3 × 10 <sup>-11</sup>	10.5
Lactic	CH <sub>3</sub> CH(OH)COOH	CH <sub>3</sub> CH(OH)COO <sup>-</sup>	1.4 × 10 <sup>-4</sup>	3.86
Methylammonium ion	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>2</sub>	2.2 × 10 <sup>-11</sup>	10.66
Oxalic	(COOH) <sub>2</sub>	HOOC CO <sub>2</sub> <sup>-</sup>	5.6 × 10 <sup>-2</sup>	1.25
Perchloric*	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	4.0 × 10 <sup>1</sup>	-1.6
Phenol	C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	1.0 × 10 <sup>-10</sup>	9.99
Phosphoric	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	6.9 × 10 <sup>-3</sup>	2.16
Propanoic	CH <sub>3</sub> CH <sub>2</sub> COOH	CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup>	1.4 × 10 <sup>-5</sup>	4.87
Pyridinium ion	C <sub>5</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> N	5.9 × 10 <sup>-6</sup>	5.23
Sulfuric	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	10 <sup>2</sup>	-2
Sulfurous	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	1.4 × 10 <sup>-2</sup>	1.85
Triethylammonium ion	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sup>+</sup>	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	1.8 × 10 <sup>-11</sup>	10.75
Trimethylammonium ion	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	(CH <sub>3</sub> ) <sub>3</sub> N	1.6 × 10 <sup>-10</sup>	9.80

\* At 293 K.

**Table 9.2** The error function

<i>z</i>	<i>erf z</i>	<i>z</i>	<i>erf z</i>
0	0	0.45	0.475 48
0.01	0.011 28	0.50	0.520 50
0.02	0.022 56	0.55	0.563 32
0.03	0.033 84	0.60	0.603 86
0.04	0.045 11	0.65	0.642 03
0.05	0.056 37	0.70	0.677 80
0.06	0.067 62	0.75	0.711 16
0.07	0.078 86	0.80	0.742 10
0.08	0.090 08	0.85	0.770 67
0.09	0.101 28	0.90	0.796 91
0.10	0.112 46	0.95	0.820 89
0.15	0.168 00	1.00	0.842 70
0.20	0.222 70	1.20	0.910 31
0.25	0.276 32	1.40	0.952 28
0.30	0.328 63	1.60	0.976 35
0.35	0.379 38	1.80	0.989 09
0.40	0.428 39	2.00	0.995 32

Data: AS.

**Table 10.2** Screening constants for atoms; values of  $Z_{\text{eff}} = Z - \sigma$  for neutral ground-state atoms

H								He
1s	1							1.6875
	Li	Be	B	C	N	O	F	Ne
1s	2.6906	3.6848	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
2s	1.2792	1.9120	2.5762	3.2166	3.8474	4.4916	5.1276	5.7584
2p			2.4214	3.1358	3.8340	4.4532	5.1000	5.7584
	Na	Mg	Al	Si	P	S	Cl	Ar
1s	10.6259	11.6089	12.5910	13.5745	14.5578	15.5409	16.5239	17.5075
2s	6.5714	7.3920	8.3736	9.0200	9.8250	10.6288	11.4304	12.2304
2p	6.8018	7.8258	8.9634	9.9450	10.9612	11.9770	12.9932	14.0082
3s	2.5074	3.3075	4.1172	4.9032	5.6418	6.3669	7.0683	7.7568
3p			4.0656	4.2852	4.8864	5.4819	6.1161	6.7641

Data: E. Clementi and D.L. Raimondi, *Atomic screening constants from SCF functions*. IBM Res. Note NJ-27 (1963). *J. chem. Phys.* **38**, 2686 (1963).

**Table 10.3** Ionization energies,  $I/(kJ\ mol^{-1})$ 

H							He
1312.0							2372.3
							5250.4
Li	Be	B	C	N	O	F	Ne
513.3	899.4	800.6	1086.2	1402.3	1313.9	1681	2080.6
7298.0	1757.1	2427	2352	2856.1	3388.2	3374	3952.2
Na	Mg	Al	Si	P	S	Cl	Ar
495.8	737.7	577.4	786.5	1011.7	999.6	1251.1	1520.4
4562.4	1450.7	1816.6	1577.1	1903.2	2251	2297	2665.2
		2744.6		2912			
K	Ca	Ga	Ge	As	Se	Br	Kr
418.8	589.7	578.8	762.1	947.0	940.9	1139.9	1350.7
3051.4	1145	1979	1537	1798	2044	2104	2350
		2963	2735				
Rb	Sr	In	Sn	Sb	Te	I	Xe
403.0	549.5	558.3	708.6	833.7	869.2	1008.4	1170.4
2632	1064.2	1820.6	1411.8	1794	1795	1845.9	2046
		2704	2943.0	2443			
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
375.5	502.8	589.3	715.5	703.2	812	930	1037
2420	965.1	1971.0	1450.4	1610			
		2878	3081.5	2466			

Data: E.

**Table 10.4** Electron affinities,  $E_{ea}/(kJ\ mol^{-1})$ 

H							He
72.8							-21
Li	Be	B	C	N	O	F	Ne
59.8	≤0	23	122.5	-7	141	322	-29
					-844		
Na	Mg	Al	Si	P	S	Cl	Ar
52.9	≤0	44	133.6	71.7	200.4	348.7	-35
					-532		
K	Ca	Ga	Ge	As	Se	Br	Kr
48.3	2.37	36	116	77	195.0	324.5	-39
Rb	Sr	In	Sn	Sb	Te	I	Xe
46.9	5.03	34	121	101	190.2	295.3	-41
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
45.5	13.95	30	35.2	101	186	270	-41

Data: E.

**Table 11.2** Bond lengths,  $R_c$ /pm

## (a) Bond lengths in specific molecules

$\text{Br}_2$	228.3
$\text{Cl}_2$	198.75
CO	112.81
$\text{F}_2$	141.78
$\text{H}_2^+$	106
$\text{H}_2$	74.138
HBr	141.44
HCl	127.45
HF	91.680
HI	160.92
$\text{N}_2$	109.76
$\text{O}_2$	120.75

## (b) Mean bond lengths from covalent radii\*

H	37						
C	77(1)	N	74(1)	O	66(1)	F	64
	67(2)		65(2)		57(2)		
	60(3)						
Si	118	P	110	S	104(1)	Cl	99
					95(2)		
Ge	122	As	121	Se	104	Br	114
		Sb	141	Te	137	I	133

\* Values are for single bonds except where indicated otherwise (values in parentheses). The length of an A–B covalent bond (of given order) is the sum of the corresponding covalent radii.

**Table 11.3a** Bond dissociation enthalpies,  $\Delta H^\circ(\text{A–B})/( \text{kJ mol}^{-1})$  at 298 K

## Diatomeric molecules

H–H	436	F–F	155	Cl–Cl	242	Br–Br	193	I–I	151
O=O	497	C=O	1076	N≡N	945				
H–O	428	H–F	565	H–Cl	431	H–Br	366	H–I	299

## Polyatomic molecules

H–CH <sub>3</sub>	435	H–NH <sub>2</sub>	460	H–OH	492	H–C <sub>6</sub> H <sub>5</sub>	469
H <sub>3</sub> C–CH <sub>3</sub>	368	H <sub>2</sub> C=CH <sub>2</sub>	720	HC≡CH	962		
HO–CH <sub>3</sub>	377	Cl–CH <sub>3</sub>	352	Br–CH <sub>3</sub>	293	I–CH <sub>3</sub>	237
O=CO	531	HO–OH	213	O <sub>2</sub> N–NO <sub>2</sub>	54		

Data: HCP, KL.

**Table 11.3b** Mean bond enthalpies,  $\Delta H^\circ(A-B)/(kJ\ mol^{-1})$ 

	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C	412	348(i) 612(ii) 838(iii) 518(a)									
N	388	305(i) 613(ii) 890(iii)	163(i)								
O	463	360(i) 743(ii)	157	146(i) 497(ii)							
F	565	484	270	185	155						
Cl	431	338	200	203	254	242					
Br	366	276				219	193				
I	299	238				210	178	151			
S	338	259			496	250	212		264		
P	322									201	
Si	318		374	466							226

(i) Single bond, (ii) double bond, (iii) triple bond, (a) aromatic.

Data: HCP and L. Pauling, *The nature of the chemical bond*. Cornell University Press (1960).**Table 11.4** Pauling (*italics*) and Mulliken electronegativities

H	He							
2.20								
3.06								
	Li	Be	B	C	N	O	F	Ne
	0.98	1.57	2.04	2.55	3.04	3.44	3.98	
	1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
	Na	Mg	Al	Si	P	S	Cl	Ar
	0.93	1.31	1.61	1.90	2.19	2.58	3.16	
	1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
	K	Ca	Ga	Ge	As	Se	Br	Kr
	0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
	1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
	Rb	Sr	In	Sn	Sb	Te	I	Xe
	0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
	0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
	Cs	Ba	Tl	Pb	Bi			
	0.79	0.89	2.04	2.33	2.02			

Data: Pauling values: A.L. Allred, *J. Inorg. Nucl. Chem.* **17**, 215 (1961); L.C. Allen and J.E. Huheey, *ibid.*, **42**, 1523 (1980). Mulliken values: L.C. Allen, *J. Am. Chem. Soc.* **111**, 9003 (1989). The Mulliken values have been scaled to the range of the Pauling values.

**Table 13.2** Properties of diatomic molecules

	$\tilde{\nu}_0/\text{cm}^{-1}$	$\theta_V/\text{K}$	$B/\text{cm}^{-1}$	$\theta_R/\text{K}$	$r/\text{pm}$	$k/(\text{N m}^{-1})$	$D/(\text{kJ mol}^{-1})$	$\sigma$
$^1\text{H}_2^+$	2321.8	3341	29.8	42.9	106	160	255.8	2
$^1\text{H}_2$	4400.39	6332	60.864	87.6	74.138	574.9	432.1	2
$^2\text{H}_2$	3118.46	4487	30.442	43.8	74.154	577.0	439.6	2
$^1\text{H}^{19}\text{F}$	4138.32	5955	20.956	30.2	91.680	965.7	564.4	1
$^1\text{H}^{35}\text{Cl}$	2990.95	4304	10.593	15.2	127.45	516.3	427.7	1
$^1\text{H}^{81}\text{Br}$	2648.98	3812	8.465	12.2	141.44	411.5	362.7	1
$^1\text{H}^{127}\text{I}$	2308.09	3321	6.511	9.37	160.92	313.8	294.9	1
$^{14}\text{N}_2$	2358.07	3393	1.9987	2.88	109.76	2293.8	941.7	2
$^{16}\text{O}_2$	1580.36	2274	1.4457	2.08	120.75	1176.8	493.5	2
$^{19}\text{F}_2$	891.8	1283	0.8828	1.27	141.78	445.1	154.4	2
$^{35}\text{Cl}_2$	559.71	805	0.2441	0.351	198.75	322.7	239.3	2
$^{12}\text{C}^{16}\text{O}$	2170.21	3122	1.9313	2.78	112.81	1903.17	1071.8	1
$^{79}\text{Br}^{81}\text{Br}$	323.2	465	0.0809	10.116	283.3	245.9	190.2	1

Data: AIP.

**Table 13.3** Typical vibrational wavenumbers,  $\tilde{\nu}/\text{cm}^{-1}$ 

C–H stretch	2850–2960
C–H bend	1340–1465
C–C stretch, bend	700–1250
C=C stretch	1620–1680
C≡C stretch	2100–2260
O–H stretch	3590–3650
H-bonds	3200–3570
C=O stretch	1640–1780
C≡N stretch	2215–2275
N–H stretch	3200–3500
C–F stretch	1000–1400
C–Cl stretch	600–800
C–Br stretch	500–600
C–I stretch	500
$\text{CO}_3^{2-}$	1410–1450
$\text{NO}_3^-$	1350–1420
$\text{NO}_2^-$	1230–1250
$\text{SO}_4^{2-}$	1080–1130
Silicates	900–1100

Data: L.J. Bellamy, *The infrared spectra of complex molecules and Advances in infrared group frequencies*. Chapman and Hall.**Table 14.1** Colour, frequency, and energy of light

Colour	$\lambda/\text{nm}$	$\nu/(10^{14} \text{ Hz})$	$\tilde{\nu}/(10^4 \text{ cm}^{-1})$	$E/\text{eV}$	$E/(\text{kJ mol}^{-1})$
Infrared	>1000	<3.00	<1.00	<1.24	<120
Red	700	4.28	1.43	1.77	171
Orange	620	4.84	1.61	2.00	193
Yellow	580	5.17	1.72	2.14	206
Green	530	5.66	1.89	2.34	226
Blue	470	6.38	2.13	2.64	254
Violet	420	7.14	2.38	2.95	285
Near ultraviolet	300	10.0	3.33	4.15	400
Far ultraviolet	<200	>15.0	>5.00	>6.20	>598

Data: J.G. Calvert and J.N. Pitts, *Photochemistry*. Wiley, New York (1966).

**Table 14.3** Absorption characteristics of some groups and molecules

Group	$\tilde{\nu}_{\text{max}}/(10^4 \text{ cm}^{-1})$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
$\text{C}=\text{C} (\pi^* \leftarrow \pi)$	6.10	163	$1.5 \times 10^4$
	5.73	174	$5.5 \times 10^3$
$\text{C}=\text{O} (\pi^* \leftarrow n)$	3.7–3.5	270–290	10–20
	2.9	350	15
$-\text{N}=\text{N}-$	>3.9	<260	Strong
	3.6	280	10
$-\text{NO}_2$	4.8	210	$1.0 \times 10^4$
	3.6	255	200
$\text{C}_6\text{H}_5-$	5.0	200	$6.3 \times 10^3$
	5.5	180	$1.0 \times 10^5$
	3.9	167	$7.0 \times 10^3$
$[\text{Cu}(\text{OH}_2)_6]^{2+}(\text{aq})$	1.2	810	10
$[\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$	1.7	600	50
$\text{H}_2\text{O} (\pi^* \leftarrow n)$			

**Table 15.2** Nuclear spin properties

Nuclide	Natural abundance %	Spin $I$	Magnetic moment $\mu/\mu_N$	g-value	$\gamma/(10^7 \text{ T}^{-1} \text{ s}^{-1})$	NMR frequency at 1 T, $\nu/\text{MHz}$
${}^1\text{n}^*$		$\frac{1}{2}$	-1.9130	-3.8260	-18.324	29.164
${}^1\text{H}$	99.9844	$\frac{1}{2}$	2.792 85	5.5857	26.752	42.576
${}^2\text{H}$	0.0156	1	0.857 44	0.857 45	4.1067	6.536
${}^3\text{H}^*$		$\frac{1}{2}$	2.978 96	-4.2553	-20.380	45.414
${}^{10}\text{B}$	19.6	3	1.8006	0.6002	2.875	4.575
${}^{11}\text{B}$	80.4	$\frac{3}{2}$	2.6886	1.7923	8.5841	13.663
${}^{13}\text{C}$	1.108	$\frac{1}{2}$	0.7024	1.4046	6.7272	10.708
${}^{14}\text{N}$	99.635	1	0.403 76	0.403 56	1.9328	3.078
${}^{17}\text{O}$	0.037	$\frac{5}{2}$	-1.893 79	-0.7572	-3.627	5.774
${}^{19}\text{F}$	100	$\frac{1}{2}$	2.628 87	5.2567	25.177	40.077
${}^{31}\text{P}$	100	$\frac{1}{2}$	1.1316	2.2634	10.840	17.251
${}^{33}\text{S}$	0.74	$\frac{3}{2}$	0.6438	0.4289	2.054	3.272
${}^{35}\text{Cl}$	75.4	$\frac{3}{2}$	0.8219	0.5479	2.624	4.176
${}^{37}\text{Cl}$	24.6	$\frac{3}{2}$	0.6841	0.4561	2.184	3.476

\* Radioactive.

$\mu$  is the magnetic moment of the spin state with the largest value of  $m_I$ ;  $\mu = g_I \mu_N I$  and  $\mu_N$  is the nuclear magneton (see inside front cover).  
Data: KL and HCP.

**Table 15.3** Hyperfine coupling constants for atoms,  $a/\text{mT}$ 

Nuclide	Spin	Isotropic coupling	Anisotropic coupling
$^1\text{H}$	$\frac{1}{2}$	50.8(1s)	
$^2\text{H}$	1	7.8(1s)	
$^{13}\text{C}$	$\frac{1}{2}$	113.0(2s)	6.6(2p)
$^{14}\text{N}$	1	55.2(2s)	4.8(2p)
$^{19}\text{F}$	$\frac{1}{2}$	1720(2s)	108.4(2p)
$^{31}\text{P}$	$\frac{1}{2}$	364(3s)	20.6(3p)
$^{35}\text{Cl}$	$\frac{3}{2}$	168(3s)	10.0(3p)
$^{37}\text{Cl}$	$\frac{3}{2}$	140(3s)	8.4(3p)

Data: P.W. Atkins and M.C.R. Symons, *The structure of inorganic radicals*. Elsevier, Amsterdam (1967).**Table 18.1** Dipole moments, polarizabilities, and polarizability volumes

	$\mu/(10^{-30} \text{ C m})$	$\mu/\text{D}$	$\alpha/(10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2)$	$\alpha'/(10^{-30} \text{ m}^3)$
Ar	0	0	1.66	1.85
$\text{C}_2\text{H}_5\text{OH}$	5.64	1.69		
$\text{C}_6\text{H}_5\text{CH}_3$	1.20	0.36		
$\text{C}_6\text{H}_6$	0	0	10.4	11.6
$\text{CCl}_4$	0	0	10.3	11.7
$\text{CH}_2\text{Cl}_2$	5.24	1.57	6.80	7.57
$\text{CH}_3\text{Cl}$	6.24	1.87	4.53	5.04
$\text{CH}_3\text{OH}$	5.70	1.71	3.23	3.59
$\text{CH}_4$	0	0	2.60	2.89
$\text{CHCl}_3$	3.37	1.01	8.50	9.46
CO	0.390	0.117	1.98	2.20
$\text{CO}_2$	0	0	2.63	2.93
$\text{H}_2$	0	0	0.819	0.911
$\text{H}_2\text{O}$	6.17	1.85	1.48	1.65
HBr	2.67	0.80	3.61	4.01
HCl	3.60	1.08	2.63	2.93
He	0	0	0.20	0.22
HF	6.37	1.91	0.51	0.57
HI	1.40	0.42	5.45	6.06
$\text{N}_2$	0	0	1.77	1.97
$\text{NH}_3$	4.90	1.47	2.22	2.47
1,2-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	2.07	0.62		

Data: HCP and C.J.F. Böttcher and P. Bordewijk, *Theory of electric polarization*. Elsevier, Amsterdam (1978).

**Table 18.4** Lennard-Jones (12,6)-potential parameters

	$(\epsilon/k)/K$	$r_0/\text{pm}$
Ar	111.84	362.3
$\text{C}_2\text{H}_2$	209.11	463.5
$\text{C}_2\text{H}_4$	200.78	458.9
$\text{C}_2\text{H}_6$	216.12	478.2
$\text{C}_6\text{H}_6$	377.46	617.4
$\text{CCl}_4$	378.86	624.1
$\text{Cl}_2$	296.27	448.5
$\text{CO}_2$	201.71	444.4
$\text{F}_2$	104.29	357.1
Kr	154.87	389.5
$\text{N}_2$	91.85	391.9
$\text{O}_2$	113.27	365.4
Xe	213.96	426.0

Source: F. Cuadros, I. Cachadiña, and W. Ahamuda, *Molec. Engineering*, **6**, 319 (1996).

**Table 18.5** Surface tensions of liquids at 293 K

	$\gamma/(\text{mN m}^{-1})$
Benzene	28.88
Carbon tetrachloride	27.0
Ethanol	22.8
Hexane	18.4
Mercury	472
Methanol	22.6
Water	72.75
	72.0 at 25°C
	58.0 at 100°C

Data: KL.

**Table 19.1** Radius of gyration of some macromolecules

	$M/(\text{kg mol}^{-1})$	$R_g/\text{nm}$
Serum albumin	66	2.98
Myosin	493	46.8
Polystyrene	$3.2 \times 10^3$	50 (in poor solvent)
DNA	$4 \times 10^3$	117.0
Tobacco mosaic virus	$3.9 \times 10^4$	92.4

Data: C. Tanford, *Physical chemistry of macromolecules*. Wiley, New York (1961).

**Table 19.2** Diffusion coefficients of macromolecules in water at 20°C

	$M/(\text{kg mol}^{-1})$	$D/(10^{-10} \text{ m}^2 \text{ s}^{-1})$
Sucrose	0.342	4.586
Ribonuclease	13.7	1.19
Lysozyme	14.1	1.04
Serum albumin	65	0.594
Haemoglobin	68	0.69
Urease	480	0.346
Collagen	345	0.069
Myosin	493	0.116

Data: C. Tanford, *Physical chemistry of macromolecules*. Wiley, New York (1961).

**Table 19.3** Frictional coefficients and molecular geometry

Major axis/Minor axis	Prolate	Oblate
2	1.04	1.04
3	1.11	1.10
4	1.18	1.17
5	1.25	1.22
6	1.31	1.28
7	1.38	1.33
8	1.43	1.37
9	1.49	1.42
10	1.54	1.46
50	2.95	2.38
100	4.07	2.97

Data: K.E. Van Holde, *Physical biochemistry*. Prentice-Hall, Englewood Cliffs (1971).

Sphere; radius  $a$ ,  $c = af_0$

Prolate ellipsoid; major axis  $2a$ , minor axis  $2b$ ,  $c = (ab^2)^{1/3}$

$$f = \left\{ \frac{(1 - b^2/a^2)^{1/2}}{(b/a)^{2/3} \ln \{ [1 + (1 - b^2/a^2)^{1/2}] / (b/a) \}} \right\} f_0$$

Oblate ellipsoid; major axis  $2a$ , minor axis  $2b$ ,  $c = (a^2b)^{1/3}$

$$f = \left\{ \frac{(a^2/b^2 - 1)^{1/2}}{(a/b)^{2/3} \arctan [(a^2/b^2 - 1)^{1/2}]} \right\} f_0$$

Long rod; length  $l$ , radius  $a$ ,  $c = (3a^2/4)^{1/3}$

$$f = \left\{ \frac{(1/2a)^{2/3}}{(3/2)^{1/3} \{ 2 \ln(l/a) - 0.11 \}} \right\} f_0$$

In each case  $f_0 = 6\pi\eta c$  with the appropriate value of  $c$ .

**Table 19.4** Intrinsic viscosity

Macromolecule	Solvent	$\theta/^\circ\text{C}$	$K/(10^{-3} \text{ cm}^3 \text{ g}^{-1})$	$a$
Polystyrene	Benzene	25	9.5	0.74
	Cyclohexane	34†	81	0.50
Polyisobutylene	Benzene	23†	83	0.50
	Cyclohexane	30	26	0.70
Amylose	0.33 M KCl(aq)	25†	113	0.50
Various proteins‡	Guanidine hydrochloride + HSCH <sub>2</sub> CH <sub>2</sub> OH		7.16	0.66

† The  $\theta$  temperature.

‡ Use  $[\eta] = KN^a$ ;  $N$  is the number of amino acid residues.

Data: K.E. Van Holde, *Physical biochemistry*. Prentice-Hall, Englewood Cliffs (1971).

**Table 20.3** Ionic radii ( $r/\text{pm}$ )†

Li <sup>+</sup> (4)	Be <sup>2+</sup> (4)	B <sup>3+</sup> (4)	N <sup>3-</sup>	O <sup>2-</sup> (6)	F <sup>-</sup> (6)		
59	27	12	171	140	133		
Na <sup>+</sup> (6)	Mg <sup>2+</sup> (6)	Al <sup>3+</sup> (6)	P <sup>3-</sup>	S <sup>2-</sup> (6)	Cl <sup>-</sup> (6)		
102	72	53	212	184	181		
K <sup>+</sup> (6)	Ca <sup>2+</sup> (6)	Ga <sup>3+</sup> (6)	As <sup>3-</sup> (6)	Se <sup>2-</sup> (6)	Br <sup>-</sup> (6)		
138	100	62	222	198	196		
Rb <sup>+</sup> (6)	Sr <sup>2+</sup> (6)	In <sup>3+</sup> (6)		Te <sup>2-</sup> (6)	I <sup>-</sup> (6)		
149	116	79		221	220		
Cs <sup>+</sup> (6)	Ba <sup>2+</sup> (6)	Tl <sup>3+</sup> (6)					
167	136	88					
<i>d</i> -block elements (high-spin ions)							
Sc <sup>3+</sup> (6)	Ti <sup>4+</sup> (6)	Cr <sup>3+</sup> (6)	Mn <sup>3+</sup> (6)	Fe <sup>2+</sup> (6)	Co <sup>3+</sup> (6)	Cu <sup>2+</sup> (6)	Zn <sup>2+</sup> (6)
73	60	61	65	63	61	73	75

† Numbers in parentheses are the coordination numbers of the ions. Values for ions without a coordination number stated are estimates.

Data: R.D. Shannon and C.T. Prewitt, *Acta Cryst.* **B25**, 925 (1969).

**Table 20.5** Lattice enthalpies,  $\Delta H_L^\ominus$ /(kJ mol<sup>-1</sup>)

	F	Cl	Br	I
<b>Halides</b>				
Li	1037	852	815	761
Na	926	787	752	705
K	821	717	689	649
Rb	789	695	668	632
Cs	750	676	654	620
Ag	969	912	900	886
Be		3017		
Mg		2524		
Ca		2255		
Sr		2153		
<b>Oxides</b>				
MgO	3850	CaO	3461	SrO
			3283	BaO
				3114
<b>Sulfides</b>				
MgS	3406	CaS	3119	SrS
			2974	BaS
				2832

Entries refer to MX(s) → M<sup>+</sup>(g) + X<sup>-</sup>(g).Data: Principally D. Cubicciotti, *J. Chem. Phys.* **31**, 1646 (1959).**Table 20.6** Magnetic susceptibilities at 298 K

	$\chi/10^{-6}$	$\chi_m/(10^{-4} \text{ cm}^3 \text{ mol}^{-1})$
Water	-90	-16.0
Benzene	-7.2	-6.4
Cyclohexane	-7.9	-8.5
Carbon tetrachloride	-8.9	-8.4
NaCl(s)	-13.9	-3.75
Cu(s)	-96	-6.8
S(s)	-12.9	-2.0
Hg(l)	-28.5	-4.2
CuSO <sub>4</sub> ·5H <sub>2</sub> O(s)	+176	+192
MnSO <sub>4</sub> ·4H <sub>2</sub> O(s)	+2640	+2.79 × 10 <sup>3</sup>
NiSO <sub>4</sub> ·7H <sub>2</sub> O(s)	+416	+600
FeSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O(s)	+755	+1.51 × 10 <sup>3</sup>
Al(s)	+22	+2.2
Pt(s)	+262	+22.8
Na(s)	+7.3	+1.7
K(s)	+5.6	+2.5

Data: KL and  $\chi_m = \chi M/\rho$ .**Table 21.1** Collision cross-sections,  $\sigma/\text{nm}^2$ 

Ar	0.36
C <sub>2</sub> H <sub>4</sub>	0.64
C <sub>6</sub> H <sub>6</sub>	0.88
CH <sub>4</sub>	0.46
Cl <sub>2</sub>	0.93
CO <sub>2</sub>	0.52
H <sub>2</sub>	0.27
He	0.21
N <sub>2</sub>	0.43
Ne	0.24
O <sub>2</sub>	0.40
SO <sub>2</sub>	0.58

Data: KL.

**Table 21.2** Transport properties of gases at 1 atm

	$\kappa/(J \text{ K}^{-1} \text{ m}^{-1} \text{ s}^{-1})$	$\eta/\mu P$	
	273 K	273 K	293 K
Air	0.0241	173	182
Ar	0.0163	210	223
C <sub>2</sub> H <sub>4</sub>	0.0164	97	103
CH <sub>4</sub>	0.0302	103	110
Cl <sub>2</sub>	0.079	123	132
CO <sub>2</sub>	0.0145	136	147
H <sub>2</sub>	0.1682	84	88
He	0.1442	187	196
Kr	0.0087	234	250
N <sub>2</sub>	0.0240	166	176
Ne	0.0465	298	313
O <sub>2</sub>	0.0245	195	204
Xe	0.0052	212	228

Data: KL.

**Table 21.4** Viscosities of liquids at 298 K,  $\eta/(10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$ 

Benzene	0.601
Carbon tetrachloride	0.880
Ethanol	1.06
Mercury	1.55
Methanol	0.553
Pentane	0.224
Sulfuric acid	27
Water†	0.891

† The viscosity of water over its entire liquid range is represented with less than 1 per cent error by the expression

$$\log(\eta_{20}/\eta) = A/B,$$

$$A = 1.37023(t - 20) + 8.36 \times 10^{-4}(t - 20)^2$$

$$B = 109 + t \quad t = \theta/\text{°C}$$

Convert  $\text{kg m}^{-1} \text{ s}^{-1}$  to centipoise (cP) by multiplying by  $10^3$  (so  $\eta \approx 1 \text{ cP}$  for water).

Data: AIP, KL.

**Table 21.5** Limiting ionic conductivities in water at 298 K,  $\lambda/(\text{mS m}^2 \text{ mol}^{-1})$ 

Cations	Anions	
$\text{Ba}^{2+}$	12.72	$\text{Br}^-$ 7.81
$\text{Ca}^{2+}$	11.90	$\text{CH}_3\text{CO}_2^-$ 4.09
$\text{Cs}^+$	7.72	$\text{Cl}^-$ 7.635
$\text{Cu}^{2+}$	10.72	$\text{ClO}_4^-$ 6.73
$\text{H}^+$	34.96	$\text{CO}_3^{2-}$ 13.86
$\text{K}^+$	7.350	$(\text{CO}_2)_2^{2-}$ 14.82
$\text{Li}^+$	3.87	$\text{F}^-$ 5.54
$\text{Mg}^{2+}$	10.60	$[\text{Fe}(\text{CN})_6]^{3-}$ 30.27
$\text{Na}^+$	5.010	$[\text{Fe}(\text{CN})_6]^{4-}$ 44.20
$[\text{N}(\text{C}_2\text{H}_5)_4]^+$	3.26	$\text{HCO}_2^-$ 5.46
$[\text{N}(\text{CH}_3)_4]^+$	4.49	$\text{I}^-$ 7.68
$\text{NH}_4^+$	7.35	$\text{NO}_3^-$ 7.146
$\text{Rb}^+$	7.78	$\text{OH}^-$ 19.91
$\text{Sr}^{2+}$	11.89	$\text{SO}_4^{2-}$ 16.00
$\text{Zn}^{2+}$	10.56	

Data: KL, RS.

**Table 21.6** Ionic mobilities in water at 298 K,  $u/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$ 

Cations	Anions
$\text{Ag}^+$	6.24
$\text{Ca}^{2+}$	6.17
$\text{Cu}^{2+}$	5.56
$\text{H}^+$	36.23
$\text{K}^+$	7.62
$\text{Li}^+$	4.01
$\text{Na}^+$	5.19
$\text{NH}_4^+$	7.63
$[\text{N}(\text{CH}_3)_4]^+$	4.65
$\text{Rb}^+$	7.92
$\text{Zn}^{2+}$	5.47
	$\text{Br}^-$ 8.09
	$\text{CH}_3\text{CO}_2^-$ 4.24
	$\text{Cl}^-$ 7.91
	$\text{CO}_3^{2-}$ 7.46
	$\text{F}^-$ 5.70
	$[\text{Fe}(\text{CN})_6]^{3-}$ 10.5
	$[\text{Fe}(\text{CN})_6]^{4-}$ 11.4
	$\text{I}^-$ 7.96
	$\text{NO}_3^-$ 7.40
	$\text{OH}^-$ 20.64
	$\text{SO}_4^{2-}$ 8.29

Data: Principally Table 21.4 and  $u = \lambda/zF$ .

**Table 21.7** Debye–Hückel–Onsager coefficients for (1,1)-electrolytes at 25°C

Solvent	$A/(\text{mS m}^2 \text{ mol}^{-1}/(\text{mol dm}^{-3})^{1/2})$	$B/(\text{mol dm}^{-3})^{-1/2}$
Acetone (propanone)	3.28	1.63
Acetonitrile	2.29	0.716
Ethanol	8.97	1.83
Methanol	15.61	0.923
Nitrobenzene	4.42	0.776
Nitromethane	111	0.708
Water	6.020	0.229

Data: J.O'M. Bockris and A.K.N. Reddy, *Modern electrochemistry*. Plenum, New York (1970).

**Table 21.8** Diffusion coefficients at 25°C,  $D/(10^{-9} \text{ m}^2 \text{ s}^{-1})$ 

Molecules in liquids			Ions in water			
I <sub>2</sub> in hexane	4.05	H <sub>2</sub> in CCl <sub>4</sub> (l)	9.75	K <sup>+</sup>	1.96	Br <sup>-</sup>
in benzene	2.13	N <sub>2</sub> in CCl <sub>4</sub> (l)	3.42	H <sup>+</sup>	9.31	Cl <sup>-</sup>
CCl <sub>4</sub> in heptane	3.17	O <sub>2</sub> in CCl <sub>4</sub> (l)	3.82	Li <sup>+</sup>	1.03	F <sup>-</sup>
Glycine in water	1.055	Ar in CCl <sub>4</sub> (l)	3.63	Na <sup>+</sup>	1.33	I <sup>-</sup>
Dextrose in water	0.673	CH <sub>4</sub> in CCl <sub>4</sub> (l)	2.89			OH <sup>-</sup>
Sucrose in water	0.5216	H <sub>2</sub> O in water	2.26			
		CH <sub>3</sub> OH in water	1.58			
		C <sub>2</sub> H <sub>5</sub> OH in water	1.24			

Data: AIP and (for the ions)  $\lambda = zuF$  in conjunction with Table 21.5.

**Table 22.1** Kinetic data for first-order reactions

	Phase	$\theta/^\circ\text{C}$	$k/\text{s}^{-1}$	$t_{1/2}$
2 N <sub>2</sub> O <sub>5</sub> → 4 NO <sub>2</sub> + O <sub>2</sub>	g	25	$3.38 \times 10^{-5}$	5.70 h
	HNO <sub>3</sub> (l)	25	$1.47 \times 10^{-6}$	131 h
	Br <sub>2</sub> (l)	25	$4.27 \times 10^{-5}$	4.51 h
C <sub>2</sub> H <sub>6</sub> → 2 CH <sub>3</sub>	g	700	$5.36 \times 10^{-4}$	21.6 min
Cyclopropane → propene	g	500	$6.71 \times 10^{-4}$	17.2 min
CH <sub>3</sub> N <sub>2</sub> CH <sub>3</sub> → C <sub>2</sub> H <sub>6</sub> + N <sub>2</sub>	g	327	$3.4 \times 10^{-4}$	34 min
Sucrose → glucose + fructose	aq(H <sup>+</sup> )	25	$6.0 \times 10^{-5}$	3.2 h

g: High pressure gas-phase limit.

Data: Principally K.J. Laidler, *Chemical kinetics*. Harper & Row, New York (1987); M.J. Pilling and P.W. Seakins, *Reaction kinetics*. Oxford University Press (1995); J. Nicholas, *Chemical kinetics*. Harper & Row, New York (1976). See also JL.

**Table 22.2** Kinetic data for second-order reactions

	Phase	$\theta/^\circ\text{C}$	$k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
2 NOBr → 2 NO + Br <sub>2</sub>	g	10	0.80
2 NO <sub>2</sub> → 2 NO + O <sub>2</sub>	g	300	0.54
H <sub>2</sub> + I <sub>2</sub> → 2 HI	g	400	$2.42 \times 10^{-2}$
D <sub>2</sub> + HCl → DH + DCl	g	600	0.141
2 I → I <sub>2</sub>	g	23	$7 \times 10^9$
	hexane	50	$1.8 \times 10^{10}$
CH <sub>3</sub> Cl + CH <sub>3</sub> O <sup>-</sup>	methanol	20	$2.29 \times 10^{-6}$
CH <sub>3</sub> Br + CH <sub>3</sub> O <sup>-</sup>	methanol	20	$9.23 \times 10^{-6}$
H <sup>+</sup> + OH <sup>-</sup> → H <sub>2</sub> O	water	25	$1.35 \times 10^{11}$
	ice	-10	$8.6 \times 10^{12}$

Data: Principally K.J. Laidler, *Chemical kinetics*. Harper & Row, New York (1987); M.J. Pilling and P.W. Seakins, *Reaction kinetics*. Oxford University Press (1995); J. Nicholas, *Chemical kinetics*. Harper & Row, New York (1976).

**Table 22.4** Arrhenius parameters

First-order reactions	$A/\text{s}^{-1}$	$E_a/(\text{kJ mol}^{-1})$
Cyclopropane $\rightarrow$ propene	$1.58 \times 10^{15}$	272
$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$	$3.98 \times 10^{13}$	160
<i>cis</i> -CHD=CHD $\rightarrow$ <i>trans</i> -CHD=CHD	$3.16 \times 10^{12}$	256
Cyclobutane $\rightarrow$ 2 C <sub>2</sub> H <sub>4</sub>	$3.98 \times 10^{13}$	261
C <sub>2</sub> H <sub>5</sub> I $\rightarrow$ C <sub>2</sub> H <sub>4</sub> + HI	$2.51 \times 10^{17}$	209
C <sub>2</sub> H <sub>6</sub> $\rightarrow$ 2 CH <sub>3</sub>	$2.51 \times 10^7$	384
2 N <sub>2</sub> O <sub>5</sub> $\rightarrow$ 4 NO <sub>2</sub> + O <sub>2</sub>	$4.94 \times 10^{13}$	103
N <sub>2</sub> O $\rightarrow$ N <sub>2</sub> + O	$7.94 \times 10^{11}$	250
C <sub>2</sub> H <sub>5</sub> $\rightarrow$ C <sub>2</sub> H <sub>4</sub> + H	$1.0 \times 10^{13}$	167
Second-order, gas-phase	$A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
O + N <sub>2</sub> $\rightarrow$ NO + N	$1 \times 10^{11}$	315
OH + H <sub>2</sub> $\rightarrow$ H <sub>2</sub> O + H	$8 \times 10^{10}$	42
Cl + H <sub>2</sub> $\rightarrow$ HCl + H	$8 \times 10^{10}$	23
2 CH <sub>3</sub> $\rightarrow$ C <sub>2</sub> H <sub>6</sub>	$2 \times 10^{10}$	ca. 0
NO + Cl <sub>2</sub> $\rightarrow$ NOCl + Cl	$4.0 \times 10^9$	85
SO + O <sub>2</sub> $\rightarrow$ SO <sub>2</sub> + O	$3 \times 10^8$	27
CH <sub>3</sub> + C <sub>2</sub> H <sub>6</sub> $\rightarrow$ CH <sub>4</sub> + C <sub>2</sub> H <sub>5</sub>	$2 \times 10^8$	44
C <sub>6</sub> H <sub>5</sub> + H <sub>2</sub> $\rightarrow$ C <sub>6</sub> H <sub>6</sub> + H	$1 \times 10^8$	ca. 25
Second-order, solution	$A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
C <sub>2</sub> H <sub>5</sub> ONa + CH <sub>3</sub> I in ethanol	$2.42 \times 10^{11}$	81.6
C <sub>2</sub> H <sub>5</sub> Br + OH <sup>-</sup> in water	$4.30 \times 10^{11}$	89.5
C <sub>2</sub> H <sub>5</sub> I + C <sub>2</sub> H <sub>5</sub> O <sup>-</sup> in ethanol	$1.49 \times 10^{11}$	86.6
CH <sub>3</sub> I + C <sub>2</sub> H <sub>5</sub> O <sup>-</sup> in ethanol	$2.42 \times 10^{11}$	81.6
C <sub>2</sub> H <sub>5</sub> Br + OH <sup>-</sup> in ethanol	$4.30 \times 10^{11}$	89.5
CO <sub>2</sub> + OH <sup>-</sup> in water	$1.5 \times 10^{10}$	38
CH <sub>3</sub> I + S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> in water	$2.19 \times 10^{12}$	78.7
Sucrose + H <sub>2</sub> O in acidic water	$1.50 \times 10^{15}$	107.9
(CH <sub>3</sub> ) <sub>3</sub> CCl solvolysis		
in water	$7.1 \times 10^{16}$	100
in methanol	$2.3 \times 10^{13}$	107
in ethanol	$3.0 \times 10^{13}$	112
in acetic acid	$4.3 \times 10^{13}$	111
in chloroform	$1.4 \times 10^4$	45
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> Br		
in benzene	91	34

Data: Principally J. Nicholas, *Chemical kinetics*. Harper & Row, New York (1976) and A.A. Frost and R.G. Pearson, *Kinetics and mechanism*. Wiley, New York (1961).

**Table 24.1** Arrhenius parameters for gas-phase reactions

	$A/(dm^3 mol^{-1} s^{-1})$			
	Experiment	Theory	$E_a/(kJ mol^{-1})$	$P$
$2 NOCl \rightarrow 2 NO + Cl_2$	$9.4 \times 10^9$	$5.9 \times 10^{10}$	102.0	0.16
$2 NO_2 \rightarrow 2 NO + O_2$	$2.0 \times 10^9$	$4.0 \times 10^{10}$	111.0	$5.0 \times 10^{-2}$
$2 ClO \rightarrow Cl_2 + O_2$	$6.3 \times 10^7$	$2.5 \times 10^{10}$	0.0	$2.5 \times 10^{-3}$
$H_2 + C_2H_4 \rightarrow C_2H_6$	$1.24 \times 10^6$	$7.4 \times 10^{11}$	180	$1.7 \times 10^{-6}$
$K + Br_2 \rightarrow KBr + Br$	$1.0 \times 10^{12}$	$2.1 \times 10^{11}$	0.0	4.8

Data: Principally M.J. Pilling and P.W. Seakins, *Reaction kinetics*. Oxford University Press (1995).**Table 24.2** Arrhenius parameters for reactions in solution. See Table 22.4**Table 25.1** Maximum observed enthalpies of physisorption,  $\Delta_{ad}H^\Theta/(kJ mol^{-1})$ 

C <sub>2</sub> H <sub>2</sub>	-38	H <sub>2</sub>	-84
C <sub>2</sub> H <sub>4</sub>	-34	H <sub>2</sub> O	-59
CH <sub>4</sub>	-21	N <sub>2</sub>	-21
Cl <sub>2</sub>	-36	NH <sub>3</sub>	-38
CO	-25	O <sub>2</sub>	-21
CO <sub>2</sub>	-25		

Data: D.O. Haywood and B.M.W. Trapnell, *Chemisorption*. Butterworth (1964).**Table 25.2** Enthalpies of chemisorption,  $\Delta_{ad}H^\Theta/(kJ mol^{-1})$ 

Adsorbate	Adsorbent (substrate)											
	Ti	Ta	Nb	W	Cr	Mo	Mn	Fe	Co	Ni	Rh	Pt
H <sub>2</sub>		-188			-188	-167	-71	-134			-117	
N <sub>2</sub>		-586						-293				
O <sub>2</sub>					-720					-494	-293	
CO	-640							-192	-176			
CO <sub>2</sub>	-682	-703	-552	-456	-339	-372	-222	-225	-146	-184		
NH <sub>3</sub>				-301				-188		-155		
C <sub>2</sub> H <sub>4</sub>		-577		-427	-427			-285		-243	-209	

Data: D.O. Haywood and B.M.W. Trapnell, *Chemisorption*. Butterworth (1964).

**Table 25.3** Activation energies of catalysed reactions

	Catalyst	$E_a/(kJ\ mol^{-1})$
$2\ HI \rightarrow H_2 + I_2$	None	184
	Au(s)	105
	Pt(s)	59
$2\ NH_3 \rightarrow N_2 + 3\ H_2$	None	350
	W(s)	162
$2\ N_2O \rightarrow 2\ N_2 + O_2$	None	245
	Au(s)	121
	Pt(s)	134
$(C_2H_5)_2O$ pyrolysis	None	224
	I <sub>2</sub> (g)	144

Data: G.C. Bond, *Heterogeneous catalysis*. Clarendon Press, Oxford (1986).

**Table 25.6** Exchange current densities and transfer coefficients at 298 K

Reaction	Electrode	$j_0/(A\ cm^{-2})$	$\alpha$
$2\ H^+ + 2\ e^- \rightarrow H_2$	Pt	$7.9 \times 10^{-4}$	
	Cu	$1 \times 10^{-6}$	
	Ni	$6.3 \times 10^{-6}$	0.58
	Hg	$7.9 \times 10^{-13}$	0.50
	Pb	$5.0 \times 10^{-12}$	
	Pt	$2.5 \times 10^{-3}$	0.58
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	Pt		
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	Pt	$4.0 \times 10^{-5}$	0.75

Data: Principally J.O'M. Bockris and A.K.N. Reddy, *Modern electrochemistry*. Plenum, New York (1970).

**Table A3.1** Refractive indices relative to air at 20°C

	434 nm	589 nm	656 nm
Benzene	1.5236	1.5012	1.4965
Carbon tetrachloride	1.4729	1.4676	1.4579
Carbon disulfide	1.6748	1.6276	1.6182
Ethanol	1.3700	1.3618	1.3605
KCl(s)	1.5050	1.4904	1.4973
Kl(s)	1.7035	1.6664	1.6581
Methanol	1.3362	1.3290	1.3277
Methylbenzene	1.5170	1.4955	1.4911
Water	1.3404	1.3330	1.3312

Data: AIP.

## Character tables

### The groups $C_1$ , $C_s$ , $C_i$

$C_1$ (1)	$E$	$h = 1$
A	1	

$C_s = C_h$ (m)	$E$	$\sigma_h$	$h = 2$
A'	1	1	$x, y, R_z$ $x^2, y^2,$ $z^2, xy$
A''	1	-1	$z, R_x, R_y$ $yz, xz$

$C_i = S_2$ ( $\bar{1}$ )	$E$	$i$	$h = 2$
A <sub>g</sub>	1	1	$R_x, R_y, R_z$ $x^2, y^2, z^2,$ $xy, xz, yz$
A <sub>u</sub>	1	-1	$x, y, z$

### The groups $C_{nv}$

$C_{2v}, 2mm$	$E$	$C_2$	$\sigma_v$	$\sigma'_v$	$h=4$
A <sub>1</sub>	1	1	1	1	$z, z^2, x^2, y^2$
A <sub>2</sub>	1	1	-1	-1	$xy$
B <sub>1</sub>	1	-1	1	-1	$x, xz$
B <sub>2</sub>	1	-1	-1	1	$y, yz$

$C_{3v}, 3m$	$E$	$2C_3$	$3\sigma_v$	$h=6$
A <sub>1</sub>	1	1	1	$z, z^2, x^2 + y^2$
A <sub>2</sub>	1	1	-1	
E	2	-1	0	$(x, y), (xy, x^2 - y^2) (xz, yz)$

$C_{4v}, 4mm$	$E$	$C_2$	$2C_4$	$2\sigma_v$	$2\sigma_d$	$h=8$
A <sub>1</sub>	1	1	1	1	1	$z, z^2, x^2 + y^2$
A <sub>2</sub>	1	1	1	-1	1	
B <sub>1</sub>	1	1	-1	1	-1	$x^2 - y^2$
B <sub>2</sub>	1	1	-1	-1	1	$xy$
E	2	-2	0	0	0	$(x, y), (xz, yz)$

$C_{5v}$	$E$	$2C_5$	$2C_5^2$	$5\sigma_v$	$h=10, \alpha=72^\circ$
A <sub>1</sub>	1	1	1	1	$z, z^2, x^2 + y^2$
A <sub>2</sub>	1	1	1	-1	
E <sub>1</sub>	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	$(x, y), (xz, yz)$
E <sub>2</sub>	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	$(xy, x^2 - y^2)$

$C_{6v}, 6mm$	$E$	$C_2$	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$	$h=12$
A <sub>1</sub>	1	1	1	1	1	1	$z, z^2, x^2 + y^2$
A <sub>2</sub>	1	1	1	1	-1	1	
B <sub>1</sub>	1	-1	1	-1	-1	1	
B <sub>2</sub>	1	-1	1	-1	1	-1	
E <sub>1</sub>	2	-2	-1	1	0	0	$(x, y), (xz, yz)$
E <sub>2</sub>	2	2	-1	-1	0	0	$(xy, x^2 - y^2)$

$C_{\infty v}$	$E$	$2C_\phi \dagger$	$\infty\sigma_v$	$h=\infty$
$A_1(\Sigma^+)$	1	1	1	$z, z^2, x^2 + y^2$
$A_2(\Sigma^-)$	1	1	-1	
$E_1(\Pi)$	2	$2 \cos \phi$	0	$(x, y), (xz, yz)$
$E_2(\Delta)$	2	$2 \cos 2\phi$	0	$(xy, x^2 - y^2)$

† There is only one member of this class if  $\phi = \pi$ .

## The groups $D_n$

$D_2, 222$	$E$	$C_2^z$	$C_2^y$	$C_2^x$	$h=4$
$A_1$	1	1	1	1	$x^2, y^2, z^2$
$B_1$	1	1	-1	-1	$z, xy$
$B_2$	1	-1	1	-1	$y, xz$
$B_3$	1	-1	-1	1	$x, yz$

$D_3, 32$	$E$	$2C_3$	$3C'_2$	$h=6$
$A_1$	1	1	1	$z^2, x^2 + y^2$
$A_2$	1	1	-1	$z$
$E$	2	-1	0	$(x, y), (xz, yz), (xy, x^2 - y^2)$

$D_4, 422$	$E$	$C_2$	$2C_4$	$2C'_2$	$2C''_2$	$h=8$
$A_1$	1	1	1	1	1	$z^2, x^2 + y^2$
$A_2$	1	1	1	-1	-1	$z$
$B_1$	1	1	-1	1	-1	$x^2 - y^2$
$B_2$	1	1	-1	-1	1	$xy$
$E$	2	-2	0	0	0	$(x, y), (xz, yz)$

## The groups $D_{nh}$

$D_{3h}, \bar{6}2m$	$E$	$\sigma_h$	$2C_3$	$2S_3$	$3C'_2$	$3\sigma_v$	$h=12$
$A'_1$	1	1	1	1	1	1	$z^2, x^2 + y^2$
$A'_2$	1	1	1	1	-1	-1	
$A''_1$	1	-1	1	-1	1	-1	
$A''_2$	1	-1	1	-1	-1	1	$z$
$E'$	2	2	-1	-1	0	0	$(x, y), (xy, x^2 - y^2)$
$E''$	2	-2	-1	1	0	0	$(xz, yz)$

$D_{4h}, 4/mmm$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	$h=16$
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	$x^2+y^2, z^2$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	$R_z$
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1	$x^2-y^2$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1	$xy$
$E_g$	2	0	-2	0	0	2	0	-2	0	0	$(xz, yz)$ $(R_x, R_y)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1	
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	$z$
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1	
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1	
$E_u$	2	0	-2	0	0	-2	0	2	0	0	$(x, y)$

$D_{5h}$	$E$	$2C_5$	$2C_5^2$	$5C_2$	$\sigma_h$	$2S_5$	$2S_5^3$	$5\sigma_v$	$h=20$	$\alpha=72^\circ$
$A'_1$	1	1	1	1	1	1	1	1	$x^2+y^2, z^2$	
$A'_2$	1	1	1	-1	1	1	1	-1	$R_z$	
$E'_1$	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	$(x, y)$	
$E'_2$	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	$(x^2-y^2, xy)$	
$A''_1$	1	1	1	1	-1	-1	-1	-1		
$A''_2$	1	1	1	-1	-1	-1	-1	1	$z$	
$E''_1$	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	-2	$-2 \cos \alpha$	$-2 \cos 2\alpha$	0	$(xz, yz)$	$(R_x, R_y)$
$E''_2$	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	-2	$-2 \cos 2\alpha$	$-2 \cos \alpha$	0		

$D_{\infty h}$	$E$	$2C_\phi$	$\infty C'_2$	$i$	$2iC_\infty$	$iC'_2$	$h=\infty$
$A_{1g}(\Sigma_g^+)$	1	1	1	1	1	1	$z^2, x^2+y^2$
$A_{1u}(\Sigma_u^+)$	1	1	1	-1	-1	-1	$z$
$A_{2g}(\Sigma_g^-)$	1	1	-1	1	1	-1	$R_z$
$A_{2u}(\Sigma_u^-)$	1	1	-1	-1	1	1	
$E_{1g}(\Pi_g)$	2	$2 \cos \phi$	0	2	$-2 \cos \phi$	0	$(xz, yz)$ $(R_x, R_y)$
$E_{1u}(\Pi_u)$	2	$2 \cos \phi$	0	-2	$2 \cos \phi$	0	$(x, y)$
$E_{2g}(\Delta_g)$	2	$2 \cos 2\phi$	0	2	$2 \cos 2\phi$	0	$(xy, x^2-y^2)$
$E_{2u}(\Delta_u)$	2	$2 \cos 2\phi$	0	-2	$-2 \cos 2\phi$	0	
:							

## The cubic groups

$T_d, \bar{4}3m$	$E$	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h=24$
A <sub>1</sub>	1	1	1	1	1	$x^2 + y^2 + z^2$
A <sub>2</sub>	1	1	1	-1	-1	
E	2	-1	2	0	0	$(3z^2 - r^2, x^2 - y^2)$
T <sub>1</sub>	3	0	-1	-1	1	$(R_x, R_y, R_z)$
T <sub>2</sub>	3	0	-1	1	-1	$(x, y, z), (xy, xz, yz)$

$O_h (m3m)$	$E$	$8C_3$	$6C_2$	$6C_2$	$3C_2 (= C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A <sub>2g</sub>	1	1	-1	-1	1	1	-1	1	1	-1	
E <sub>g</sub>	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T <sub>1g</sub>	3	0	-1	1	-1	3	1	0	-1	-1	$(R_x, R_y, R_z)$
T <sub>2g</sub>	3	0	1	-1	-1	3	-1	0	-1	1	$(xy, yz, xy)$
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1	
A <sub>2u</sub>	1	1	-1	-1	1	-1	1	-1	-1	1	
E <sub>u</sub>	2	-1	0	0	2	-2	0	1	-2	0	
T <sub>1u</sub>	3	0	-1	1	-1	-3	-1	0	1	1	$(x, y, z)$
T <sub>2u</sub>	3	0	1	-1	-1	-3	1	0	1	-1	

## The icosahedral group

$I$	$E$	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	$h=60$
A	1	1	1	1	1	$z^2 + y^2 + z^2$
T <sub>1</sub>	3	$\frac{1}{2}(1 + \sqrt{5})$	$\frac{1}{2}(1 - \sqrt{5})$	0	-1	$(x, y, z)$
T <sub>2</sub>	3	$\frac{1}{2}(1 - \sqrt{5})$	$\frac{1}{2}(1 + \sqrt{5})$	0	-1	$(R_x, R_y, R_z)$
G	4	-1	-1	1	0	
G	5	0	0	-1	1	$(2z^2 - x^2 - y^2, x^2 - y^2, xy, yz, zx)$

Further information: P.W. Atkins, M.S. Child, and C.S.G. Phillips, *Tables for group theory*. Oxford University Press (1970).

# Solutions to b) exercises

## Chapter 1

- 1.1** (a) 10.5 bar, (b) 10.4 bar.  
**1.2** (a) 1.07 bar; (b) 803 Torr.  
**1.3** 120 kPa.  
**1.4**  $2.67 \times 10^3$  kg.  
**1.5**  $1.5 \times 10^3$  Pa.  
**1.6** 115 kPa.  
**1.7**  $R = 0.082\ 061\ 5\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}$ ,  $M = 31.9987\ \text{g}\ \text{mol}^{-1}$ .  
**1.8**  $P_4$ .  
**1.9** 2.61 kg.  
**1.10** (a)  $3.14\ \text{dm}^3$ ; (b) 28.2 kPa.  
**1.11**  $16.14\ \text{g}\ \text{mol}^{-1}$ .  
**1.12**  $-270^\circ\text{C}$ .  
**1.13** (a) (i) 1.0 atm, (ii) 270 atm.  
    (b) (i) 0.99 atm, (ii) 190 atm.  
**1.14**  $a = 1.34 \times 10^{-1}\ \text{kg}\ \text{m}^5\ \text{s}^{-2}\ \text{mol}^{-2}$ ,  $b = 4.36 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$ .  
**1.15** (a) 1.12, repulsive; (b)  $2.7\ \text{dm}^3\ \text{mol}^{-1}$ .  
**1.16** (a)  $0.124\ \text{dm}^3\ \text{mol}^{-1}$ ; (b)  $0.112\ \text{dm}^3\ \text{mol}^{-1}$ .  
**1.17** (a)  $8.7\ \text{cm}^3$ ; (b)  $-0.15\ \text{dm}^3\ \text{mol}^{-1}$ .  
**1.18** (a)  $x_{\text{N}} = 0.63$ ,  $x_{\text{H}} = 0.37$ ;  
    (b)  $p_{\text{N}} = 2.5\ \text{atm}$ ,  $p_{\text{H}} = 1.5\ \text{atm}$ ;  
    (c) 4.0 atm.  
**1.19**  $b = 0.0493\ \text{dm}^3\ \text{mol}^{-1}$ ,  $r = 1.94 \times 10^{-10}\ \text{m}$ ,  $a = 3.16\ \text{dm}^6\ \text{atm}\ \text{mol}^{-2}$ .  
**1.20** (a) 1259 K; (b) 0.129 nm.  
**1.21** (a)  $p = 2.6\ \text{atm}$ ,  $T = 881\ \text{K}$ ;  
    (b)  $p = 2.2\ \text{atm}$ ,  $T = 718\ \text{K}$ ;  
    (c)  $p = 1.4\ \text{atm}$ ,  $T = 356\ \text{K}$ .  
**1.22**  $b = 1.3 \times 10^{-4}\ \text{m}^3\ \text{mol}^{-1}$ ,  $Z = 0.67$ .

## Chapter 2

- 2.1** 59 J.  
**2.2**  $-91\ \text{J}$ .  
**2.3** (a)  $\Delta U = \Delta H = 0$ ,  $q = -w = 1.62 \times 10^3\ \text{J}$ ;  
    (b)  $\Delta U = \Delta H = 0$ ,  $q = -w = 1.38 \times 10^3\ \text{J}$ ;  
    (c)  $\Delta U = \Delta H = 0$ ,  $q = w = 0$ .  
**2.4**  $p_2 = 143\ \text{kPa}$ ,  $w = 0$ ,  $q = 3.28 \times 10^3\ \text{J}$ ,  $\Delta U = 3.28 \times 10^3\ \text{J}$ .  
**2.5** (a)  $-19\ \text{J}$ ; (b)  $-52.8\ \text{J}$ .  
**2.6**  $\Delta H = q = -70.6\ \text{kJ}$ ,  $w = 5.60 \times 10^3\ \text{J}$ ,  $\Delta U = -65.0\ \text{kJ}$ .  
**2.7**  $-188\ \text{J}$ .  
**2.8** (a)  $\Delta H = q = 14.9 \times 10^3\ \text{J}$ ,  $w = -831\ \text{J}$ ,  $\Delta U = 14.1\ \text{kJ}$ .  
    (b)  $\Delta H = 14.9\ \text{kJ}$ ,  $w = 0$ ,  $\Delta U = q = 14.1\ \text{kJ}$ .  
**2.9** 200 K.  
**2.10**  $-325\ \text{J}$ .  
**2.11** 8.5 Torr.  
**2.12**  $C_{p,\text{m}} = 53\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}$ ,  $C_{V,\text{m}} = 45\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}$ .  
**2.13**  $\Delta H = q = 2.0 \times 10^3\ \text{J}\ \text{mol}^{-1}$ ,  $\Delta U = 1.6 \times 10^3\ \text{J}\ \text{mol}^{-1}$ .  
**2.14**  $q = 0$ ,  $w = -3.5 \times 10^3\ \text{J} = \Delta U$ ,  $\Delta T = -24\ \text{K}$ ,  $\Delta H = -4.5 \times 10^3\ \text{J}$ .  
**2.15**  $V_f = 0.0205\ \text{m}^3$ ,  $T_f = 279\ \text{K}$ ,  $w = -6.7 \times 10^2\ \text{J}$ .  
**2.16**  $q = \Delta H = 24.0\ \text{kJ}$ ,  $w = -1.6\ \text{kJ}$ ,  $\Delta U = 22.4\ \text{kJ}$ .  
**2.17**  $-3053.6\ \text{kJ}\ \text{mol}^{-1}$ .

- 2.18**  $-1152\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.19**  $C = 68.3\ \text{J}\ \text{K}^{-1}$ ,  $\Delta T = +64.1\ \text{K}$ .  
**2.20**  $+84.40\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.21**  $+1.90\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.22** (a)  $\Delta_r H^\ominus = -589.56\ \text{kJ}\ \text{mol}^{-1}$ ,  $\Delta_r U^\ominus = -582.13\ \text{kJ}\ \text{mol}^{-1}$ .  
    (b)  $\Delta_f H^\ominus(\text{HI}) = 26.48\ \text{kJ}\ \text{mol}^{-1}$ ,  $\Delta_f H^\ominus(\text{H}_2\text{O}) = -241.82\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.23**  $-760.3\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.24**  $+52.5\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.25**  $-566.93\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.26** (a)  $\Delta_r H^\ominus(298\ \text{K}) = -175\ \text{kJ}\ \text{mol}^{-1}$ ,  $\Delta_r U^\ominus(298\ \text{K}) = -173\ \text{kJ}\ \text{mol}^{-1}$ ;  
    (b)  $\Delta_r H^\ominus(348\ \text{K}) = -176\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.27**  $-65.49\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.28**  $-1587\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.29**  $0.48\ \text{K}\ \text{atm}^{-1}$ .  
**2.30**  $\Delta U_m = +129\ \text{J}\ \text{mol}^{-1}$ ,  $q = +7.7465\ \text{kJ}\ \text{mol}^{-1}$ ,  $w = -7.62\ \text{kJ}\ \text{mol}^{-1}$ .  
**2.31**  $1.27 \times 10^{-3}\ \text{K}^{-1}$ .  
**2.32**  $3.6 \times 10^2\ \text{atm}$ .  
**2.33**  $-41.2\ \text{J}\ \text{atm}^{-1}\ \text{mol}^{-1}$ ,  $q$  (supplied) =  $27.2 \times 10^3\ \text{J}$ .

## Chapter 3

- 3.1** (a)  $1.8 \times 10^2\ \text{J}\ \text{K}^{-1}$ ; (b)  $1.5 \times 10^2\ \text{J}\ \text{K}^{-1}$ .  
**3.2**  $152.65\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}$ .  
**3.3**  $-7.3\ \text{J}\ \text{K}^{-1}$ .  
**3.4**  $\Delta S = q = 0$ ,  $w = \Delta U = +2.75\ \text{kJ}$ ,  $\Delta H = +3.58\ \text{kJ}$ .  
**3.5**  $\Delta H_{\text{tot}} = 0$ ,  $\Delta S_{\text{tot}} = 24\ \text{J}\ \text{K}^{-1}$ .  
**3.6** (a) 0; (b)  $-230\ \text{J}$ ; (c)  $-230\ \text{J}$ ; (d)  $-5.3\ \text{K}$ ; (e)  $3.2\ \text{J}\ \text{K}^{-1}$ .  
**3.7** (a)  $104.6\ \text{J}\ \text{K}^{-1}$ ; (b)  $-104.6\ \text{J}\ \text{K}^{-1}$ .  
**3.8** (a)  $-21.0\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}$ ; (b)  $+512.0\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}$ .  
**3.9** (a)  $-212.40\ \text{kJ}\ \text{mol}^{-1}$ ; (b)  $-5798\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.10** (a)  $-212.55\ \text{kJ}\ \text{mol}^{-1}$ ; (b)  $-5798\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.11**  $-86.2\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.12**  $-197\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.13** (a)  $\Delta S(\text{gas}) = +3.0\ \text{J}\ \text{K}^{-1}$ ,  $\Delta S(\text{surroundings}) = -3.0\ \text{J}\ \text{K}^{-1}$ ,  $\Delta S(\text{total}) = 0$ ;  
    (b)  $\Delta S(\text{gas}) = +3.0\ \text{J}\ \text{K}^{-1}$ ,  $\Delta S(\text{surroundings}) = 0$ ;  $\Delta S(\text{total}) = +3.0\ \text{J}\ \text{K}^{-1}$ ;  
    (c)  $\Delta S(\text{gas}) = 0$ ,  $\Delta S(\text{surroundings}) = 0$ ,  $\Delta S(\text{total}) = 0$ .  
**3.14**  $2108.11\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.15** (a) 0.500; (b) 0.50 kJ; (c) 0.5 kJ.  
**3.16**  $-2.0\ \text{J}$ .  
**3.17**  $-42.8\ \text{J}\ \text{K}^{-1}$ .  
**3.18** 3.0 kJ.  
**3.19**  $2.71\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.20**  $-0.93\ \text{kJ}\ \text{mol}^{-1}$ .  
**3.21** 200 J.  
**3.22**  $+2.88\ \text{kJ}\ \text{mol}^{-1}$ .

## Chapter 4

- 4.1** 296 K =  $23^\circ\text{C}$ .  
**4.2**  $\Delta_{\text{fus}}S = +5.5\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}$ ,  $\Delta_{\text{fus}}H = +2.4\ \text{kJ}\ \text{mol}^{-1}$ .  
**4.3**  $25.25\ \text{kJ}\ \text{mol}^{-1}$ .  
**4.4** (a)  $31.11\ \text{kJ}\ \text{mol}^{-1}$ ; (b)  $276.9\ \text{K}$ .

- 4.5** 272 K.  
**4.6** 3.6 kg s<sup>-1</sup>.  
**4.7** Frost will sublime, 0.40 kPa or more.  
**4.8** (a) 29.1 kJ mol<sup>-1</sup>; (b) At 25°C,  $p_1 = 0.22$  atm = 168 Torr; At 60°C,  $p_1 = 0.76$  atm = 576 Torr.  
**4.9** 272.41 K.  
**4.10**  $6.73 \times 10^{-2} = 6.73$  per cent.

## Chapter 5

- 5.1** 843.5 cm<sup>3</sup>.  
**5.2** 18 cm<sup>3</sup>.  
**5.3** 8.2 × 10<sup>3</sup> kPa.  
**5.4** 1.5 × 10<sup>2</sup> kPa.  
**5.5** 270 g mol<sup>-1</sup>.  
**5.6** 178 g mol<sup>-1</sup>.  
**5.7** -0.077°C.  
**5.8**  $\Delta_{\text{mix}}G = -17.3$  J,  $\Delta_{\text{mix}}S = 6.34 \times 10^{-2}$  J K<sup>-1</sup>.  
**5.9**  $\Delta_{\text{mix}}G = -3.43$  kJ,  $\Delta_{\text{mix}}S = +11.5$  J K<sup>-1</sup>,  $\Delta_{\text{mix}}H = 0$ .  
**5.10** (a) 1:1; (b) 0.7358.  
**5.11** N<sub>2</sub>: 0.51 mmol kg<sup>-1</sup>, O<sub>2</sub>: 0.27 mmol kg<sup>-1</sup>.  
**5.12** 0.067 mol dm<sup>-3</sup>.  
**5.13** 11 kg.  
**5.14** 14.0 kg mol<sup>-1</sup>.  
**5.15**  $a_A = 0.9701$ ,  $x_A = 0.980$ .  
**5.16** -3536 J mol<sup>-1</sup>, 212 Torr.  
**5.17**  $a_A = 0.436$ ,  $a_B = 0.755$ ,  $\gamma_A = 1.98$ ,  $\gamma_B = 0.968$ .  
**5.18** 0.320.  
**5.19** (a) 45.0 kg KNO<sub>3</sub>; (b) 38.8 g Ba(NO<sub>3</sub>)<sub>2</sub>.  
**5.20** 0.661.  
**5.21** 1.3.

## Chapter 6

- 6.1**  $x_A = 0.5$ ,  $y_B = 0.5$ .  
**6.2**  $x_A = 0.653$ ,  $x_B = 0.347$ ,  $p = 73.4$  kPa.  
**6.3** (a) the solution is ideal; (b)  $y_A = 0.4582$ ,  $y_B = 0.5418$ .  
**6.4** (a) 6.4 kPa; (b)  $y_B = 0.77$ ,  $y_T = 0.23$ ; (c)  $p_{(\text{final})} = 4.5$  kPa.  
**6.5** (a)  $y_A = 0.81$ ; (b)  $x_A = 0.67$ ,  $y_A = 0.925$ .  
**6.6**  $C = 3$ .  
**6.7** (a)  $C = 1$ ,  $P = 2$ ; (b)  $C = 2$ ,  $P = 2$ .  
**6.8** (a)  $C = 2$ ,  $P = 2$ ; (b)  $F = 2$ .  
**6.11**  $x_B = 0.53$ ,  $T = T_2$ ,  $x_B = 0.82$ ,  $T = T_3$ .  
**6.13** (a)  $x_B \approx 0.53$ ; (b)  $x_{AB_2} \approx 0.8$ ; (c)  $x_{AB_2} \approx 0.6$ .  
**6.14** A solid solution with  $x(\text{ZrF}_4) = 0.24$  appears at 855°C. The solid solution continues to form, and its ZrF<sub>4</sub> content increases until it reaches  $x(\text{ZrF}_4) = 0.40$  and 820°C. At that temperature, the entire sample is solid.  
**6.17** (a) When  $x_A$  falls to 0.47, a second liquid phase appears. The amount of new phase increases as  $x_A$  falls and the amount of original phase decreases until, at  $x_A = 0.314$ , only one liquid remains.  
(b) The mixture has a single liquid phase at all compositions.

## Chapter 7

- 7.1** (a)  $\Delta_f G = 0$ ; (b)  $K = 0.16841$ ; (c)  $\Delta_f G^\circ = 4.41$  kJ mol<sup>-1</sup>.  
**7.2** (a)  $K = 0.24$ ; (b)  $\Delta_f G^\circ = 19$  kJ mol<sup>-1</sup>; (c)  $K = 2.96$ .

- 7.3** (a)  $K = 1.3 \times 10^{54}$ ,  $\Delta_f G^\circ = 308.84$  kJ mol<sup>-1</sup>;  
(b)  $K = 3.5 \times 10^{49}$ ,  $\Delta_f G^\circ = -306.52$  kJ mol<sup>-1</sup>.  
**7.4** (a) Mole fractions: A: 0.1782, B: 0.0302, C: 0.1162, D: 0.6742, Total: 0.9999; (b)  $K_x = 9.6$ ; (c)  $K = 9.6$ ; (d)  $\Delta_f G^\circ = -5.6$  kJ mol<sup>-1</sup>.  
**7.5**  $T_2 = 1.4 \times 10^3$  K.  
**7.6**  $\Delta_f H^\circ = 7.191$  kJ mol<sup>-1</sup>,  $\Delta_f S^\circ = -21$  J K<sup>-1</sup> mol<sup>-1</sup>.  
**7.7**  $\Delta G^\circ = -41.0$  kJ mol<sup>-1</sup>.  
**7.9**  $x_{\text{NO}} = 1.6 \times 10^{-2}$ .  
**7.10** (a)  $\Delta_f H^\circ = 39$  kJ mol<sup>-1</sup>; (b)  $\Delta_f H^\circ = -39$  kJ mol<sup>-1</sup>.  
**7.11** (a) At 427°C,  $K = 9.24$ , At 459°C,  $K = 31.08$ ;  
(b)  $\Delta_f G^\circ = -12.9$  kJ mol<sup>-1</sup>;  
(c)  $\Delta_f H^\circ = +161$  kJ mol<sup>-1</sup>;  
(d)  $\Delta_f S^\circ = +248$  J K<sup>-1</sup> mol<sup>-1</sup>.  
**7.12**  $T = 397$  K.  
**7.13**  $\Delta_f G^\circ = -128.8$  kJ mol<sup>-1</sup>.  
**7.14** (a) R: Ag<sub>2</sub>CrO<sub>4</sub>(s) + 2e<sup>-</sup> → 2Ag(s) + CrO<sub>4</sub><sup>2-</sup>(aq) +0.45 V  
L: Cl<sub>2</sub>(g) + 2e<sup>-</sup> → 2Cl<sup>-</sup>(aq) +1.36 V  
Overall (R-L): Ag<sub>2</sub>CrO<sub>4</sub>(s) + 2Cl<sup>-</sup>(aq)  
→ 2Ag(s) + CrO<sub>4</sub><sup>2-</sup>(aq) + Cl<sub>2</sub>(g) -0.91 V  
(b) R: Sn<sup>4+</sup>(aq) + 2e<sup>-</sup> → Sn<sup>2+</sup>(aq) +0.15 V  
L: 2Fe<sup>3+</sup>(aq) + 2e<sup>-</sup> → 2Fe<sup>2+</sup>(aq) +0.77 V  
Overall (R-L): Sn<sup>4+</sup>(aq) + 2Fe<sup>2+</sup>(aq)  
→ Sn<sup>2+</sup>(aq) + 2Fe<sup>3+</sup>(aq) -0.62 V  
(c) R: MnO<sub>2</sub>(s) + 4H<sup>+</sup>(aq) + 2e<sup>-</sup> → Mn<sup>2+</sup>(aq) + 2Fe<sup>3+</sup>(aq) +1.23 V  
L: Cu<sup>2+</sup>(aq) + 2e<sup>-</sup> → Cu(s) +0.34 V  
Overall (R-L): Cu(s) + MnO<sub>2</sub>(s) + 4H<sup>+</sup>(aq)  
→ Cu<sup>2+</sup>(aq) + Mn<sup>2+</sup>(aq) + 2H<sub>2</sub>O(l) +0.89 V  
**7.15** (a) R: 2H<sub>2</sub>O(1) + 2e<sup>-</sup> → 2OH<sup>-</sup>(aq) + H<sub>2</sub>(g) -0.83 V  
L: 2Na<sup>+</sup>(aq) + 2e<sup>-</sup> → 2Na(s) -2.71 V  
and the cell is Na(s)|Na<sup>+</sup>(aq), OH<sup>-</sup>(aq)|H<sub>2</sub>(g)|Pt +1.88 V  
(b) R: I<sub>2</sub>(s) + 2e<sup>-</sup> → 2I<sup>-</sup>(aq) +0.54 V  
L: 2H<sup>+</sup>(aq) + 2e<sup>-</sup> → H<sub>2</sub>(g) 0.00 V  
and the cell is Pt|H<sub>2</sub>(g)|H<sup>+</sup>(aq), I<sup>-</sup>(aq)|I<sub>2</sub>(s)|Pt +0.54 V  
(c) R: 2H<sup>+</sup>(aq) + 2e<sup>-</sup> → H<sub>2</sub>(g) 0.00 V  
L: 2H<sub>2</sub>O(1) + 2e<sup>-</sup> → H<sub>2</sub>(g) + 2OH<sup>-</sup>(aq) 0.083 V  
and the cell is Pt|H<sub>2</sub>(g)|H<sup>+</sup>(aq), OH<sup>-</sup>(aq)|H<sub>2</sub>(g)|Pt 0.083 V  
**7.16** (a)  $E = E^\circ - \frac{RT}{F} \ln(\gamma_L b)$ ; (b)  $\Delta_f G^\circ = -89.89$  kJ mol<sup>-1</sup>;  
(c)  $E^\circ = +0.223$  V.  
**7.17** (a)  $K = 1.7 \times 10^{16}$ ; (b)  $K = 8.2 \times 10^{-7}$ .  
**7.18** (a)  $1.4 \times 10^{-20}$ ; (b)  $5.2 \times 10^{-98}$ .

## Chapter 8

- 8.1**  $v = 1.3 \times 10^{-5}$  m s<sup>-1</sup>.  
**8.2**  $p = 1.89 \times 10^{-27}$  kg m s<sup>-1</sup>,  $v = 0.565$  m s<sup>-1</sup>.  
**8.3**  $\Delta x = 5.8 \times 10^{-6}$  m.  
**8.4** (a)  $E = 0.93 \times 10^{-19}$  J,  $E$  (per mole) = 598 kJ mol<sup>-1</sup>;  
(b)  $E = 1.32 \times 10^{-15}$  J,  $E$  (per mole) = 7.98 × 10<sup>5</sup> kJ mol<sup>-1</sup>;  
(c)  $E = 1.99 \times 10^{-23}$  J,  $E$  (per mole) = 0.012 kJ mol<sup>-1</sup>.  
**8.5** (a)  $v = 0.499$  m s<sup>-1</sup>; (b)  $v = 665$  m s<sup>-1</sup>; (c)  $v = 9.98 \times 10^{-6}$  m s<sup>-1</sup>.  
**8.6**  $v = 158$  m s<sup>-1</sup>.  
**8.7** (a)  $3.52 \times 10^{17}$  s<sup>-1</sup>; (b)  $3.52 \times 10^{18}$  s<sup>-1</sup>.  
**8.8** (a) 0; (b)  $E_K = 6.84 \times 10^{-19}$  J;  $v = 1.23 \times 10^6$  m s<sup>-1</sup>.  
**8.9** (a)  $E = 2.65 \times 10^{-19}$  J, or 160 kJ mol<sup>-1</sup>; (b)  $E = 3.00 \times 10^{-19}$  J, or 181 kJ mol<sup>-1</sup>; (c)  $E = 6.62 \times 10^{-31}$  J, or 4.0 × 10<sup>-10</sup> kJ mol<sup>-1</sup>.  
**8.10** (a)  $\lambda = 1.23 \times 10^{-10}$  m; (b)  $\lambda = 3.9 \times 10^{-11}$  m; (c)  $\lambda = 3.88 \times 10^{-11}$  m.  
**8.12**  $\Delta x = 100$  pm, speed ( $\Delta v$ ):  $5.8 \times 10^5$  m s<sup>-1</sup>.

9.13  $1.67 \times 10^{-16}$  J.9.14  $\hbar$ .**Chapter 9**9.1 (a)  $2.14 \times 10^{-19}$  J, 1.34 eV,  $1.08 \times 10^4$  cm $^{-1}$ , 129 kJ mol $^{-1}$ ; (b)  $3.48 \times 10^{-19}$  J, 2.17 eV,  $1.75 \times 10^4$  cm $^{-1}$ , 210 kJ mol $^{-1}$ .9.2 (a)  $P = 0.031$ ; (b)  $P = 0.029$ .

$$9.3 p = 0, p^2 = \frac{h^2}{L^2}.$$

$$9.4 L = \left( \frac{3}{8} \right)^{1/2} \frac{h}{mc} = \left( \frac{3}{8} \right)^{1/2} \lambda_c.$$

$$9.5 x = \frac{L}{10}, \frac{3L}{10}, \frac{L}{2}, \frac{7L}{10}, \frac{9L}{10}.$$

9.6 6.

9.7  $n = 7.26 \times 10^{10}$ ,  $\Delta E = 1.71 \times 10^{-31}$  J, m = 27.5 pm, the particle behaves classically.9.8  $E_0 = 3.92 \times 10^{-21}$  J.9.9  $k = 260$  N m $^{-1}$ .9.10  $\lambda = 13.2$   $\mu\text{m}$ .9.11  $\lambda = 18.7$   $\mu\text{m}$ .9.12 (a)  $\Delta E = 2.2 \times 10^{-29}$  J; (b)  $\Delta E = 3.14 \times 10^{-20}$  J.9.14  $0, \pm 0.96\alpha$ , or  $\pm 2.02\alpha$ .9.15  $E_0 = 2.3421 \times 10^{-20}$  J.9.17 Magnitude =  $2.58 \times 10^{-34}$  J s; possible projections =  $0, \pm 1.0546 \times 10^{-34}$  J s and  $\pm 2.1109 \times 10^{-34}$  J s.**Chapter 10**10.1  $I = 12.1$  eV.10.2  $r = 11.5a_0/Z$ ,  $r = 3.53a_0/Z$ ,  $r = 0$ .10.3  $r = 0$ ,  $r = 1.382a_0$ ,  $r = 3.618a_0$ .

$$10.4 N = \frac{1}{4\sqrt{2\pi a_0^3}}.$$

$$10.5 \langle V \rangle = -\frac{Z^2 e^2}{16\pi\epsilon_0 a_0}, \langle E_K \rangle = \frac{\hbar^2 Z^2}{8ma_0^2}.$$

$$10.6 P_{3s} = 4\pi r^2 \left( \frac{1}{4\pi} \right) \times \left( \frac{1}{243} \right) \times \left( \frac{Z}{\alpha_0} \right)^3 \times (6 - 6\rho + \rho^2)^2 e^{-\rho},$$

 $r = 0.74 a_0/Z, 4.19 a_0/Z$  and  $13.08 a_0/Z$ .
10.7  $r = 1.76 a_0/Z$ .10.8 (a) angular momentum =  $6\frac{1}{2}\hbar = 2.45 \times 10^{-34}$  J s, angular nodes = 2, radial nodes = 1;(b) angular momentum =  $2\frac{1}{2}\hbar = 1.49 \times 10^{-34}$  J s, angular nodes = 1, radial nodes = 0;(c) angular momentum =  $2\frac{1}{2}\hbar = 1.49 \times 10^{-34}$  J s, angular nodes = 1, radial nodes = 1.10.9 (a)  $j = \frac{1}{2}, \frac{3}{2}$ ; (b)  $j = \frac{9}{2}, \frac{11}{2}$ .10.10  $J = 8, 7, 6, 5, 4, 3, 2$ .10.11 (a)  $g = 1$ ; (b)  $g = 64$ ; (c)  $g = 25$ .10.12 The letter F indicates that the total orbital angular momentum quantum number  $L$  is 3; the superscript 3 is the multiplicity of the term,  $2S + 1$ , related to the spin quantum number  $S = 1$ ; and the subscript 4 indicates the total angular momentum quantum number  $J$ .10.13 (a)  $r = 110$  pm,  $r = 20.1$  ppm; (b)  $r = 86$  pm,  $r = 29.4$  pm.

10.14 (a) forbidden; (b) allowed; (c) forbidden.

10.15 (a) [Ar]3d $^3$ ; (b) For  $S = \frac{3}{2}$ ,  $M_s = \pm \frac{1}{2}$  and  $\pm \frac{3}{2}$ , for  $S = \frac{1}{2}$ ,  $M_s = \pm \frac{1}{2}$ .10.16 (a)  $S = 2, 1, 0$ ; multiplicities = 5, 3, 1, respectively. (b)  $S' = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$ ; multiplicities = 6, 4, 2 respectively.10.17  $^1\text{F}_3, ^3\text{F}_4; ^3\text{F}_3; ^3\text{F}_2; ^1\text{D}_2; ^3\text{D}_3; ^3\text{D}_2; ^3\text{D}_1; ^1\text{P}_1; ^3\text{P}_2; ^3\text{P}_1; ^3\text{P}_0$ , the  $^3\text{F}_2$  set of terms are the lower in energy.10.18 (a)  $J = 3, 2$  and 1, with 7, 5 and 3 states respectively;(b)  $J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$ , with 8, 6, 4 and 2 states respectively;(c)  $J = \frac{9}{2}, \frac{7}{2}$ , with 10 and 8 states respectively.10.19 (a)  $^2\text{D}_{5/2}$  and  $^2\text{D}_{3/2}$  (b)  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$ .**Chapter 11**11.1 (a)  $1\sigma^2 2\sigma^{*1}$ ; (b)  $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ ; (c)  $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$ .11.2 (a)  $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$ ; (b)  $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ ; (c)  $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}$ .11.3 (a)  $\text{C}_2$  and  $\text{CN}$ ; (b)  $\text{NO}$ ,  $\text{O}_2$  and  $\text{F}_2$ .11.4  $\text{BrCl}$  is likely to have a shorter bond length than  $\text{BrCl}^-$ ; it has a bond order of 1, while  $\text{BrCl}^-$  has a bond order of 1/2.11.5 The sequence  $\text{O}_2^+, \text{O}_2, \text{O}_2^-, \text{O}_2^{2-}$  has progressively longer bonds.

$$11.6 N = \left( \frac{1}{1 + 2\lambda S + \lambda^2} \right)^{1/2}.$$

$$11.7 a = -\frac{0.145S + 0.844}{0.145 + 0.844S} b, N(0.844A - 0.145B).$$

11.8 Not appropriate.

$$11.9 E_{\text{trial}} = \frac{-\mu e^4}{12\pi^3 \epsilon_0^2 \hbar^2}.$$

11.10  $3.39 \times 10^{-16}$  J.11.12 (a)  $a_{2u}^2 e_{1g}^4 e_{2u}^1, E = 7\alpha + 7\beta$ ; (b)  $a_{2u}^2 e_{1g}^3, E = 5\alpha + 7\beta$ .11.13 (a) 19.31368 $\beta$ ; (b) 19.44824 $\beta$ .**Chapter 12**12.1  $\text{CCl}_4$  has 4  $C_3$  axes (each C–Cl axis), 3  $C_2$  axes (bisecting Cl–C–Cl angles), 3  $S_4$  axes (the same as the  $C_2$  axes), and 6 dihedral mirror planes (each Cl–C–Cl plane).12.2 (a)  $\text{CH}_3\text{Cl}$ .

12.3 Yes, it is zero.

12.4 Forbidden.

12.6  $T_d$  has  $S_4$  axes and mirror planes ( $= S_1$ ),  $T_h$  has a centre of inversion ( $= S_2$ ).12.8 (a)  $C_{\infty V}$ ; (b)  $D_3$ ; (c)  $C_{4V}, C_{2V}$ ; (d)  $C_s$ .12.9 (a)  $D_{2h}$ ; (b)  $D_{2h}$ ; (c) (i)  $C_{2v}$ ; (ii)  $C_{2v}$ ; (iii)  $D_{2h}$ .12.10 (a)  $C_{\infty V}$ ; (b)  $D_{5h}$ ; (c)  $C_{2v}$ ; (d)  $D_{3h}$ ; (e)  $O_h$ ; (f)  $T_d$ .12.11 (a) *ortho*-dichlorobenzene, *meta*-dichlorobenzene, HF and  $\text{XeO}_2\text{F}_2$ ; (b) none are chiral.12.12  $\text{NO}_3^-$ :  $p_x$  and  $p_y$ ,  $\text{SO}_3^-$ : all  $d$  orbitals except  $d_{z^2}$ .12.13  $A_2$ .12.14 (a)  $\text{B}_{3U}$ (x-polarized),  $\text{B}_{2U}$ (y-polarized),  $\text{B}_{1U}$ (z-polarized); (b)  $A_{1U}$  or  $E_{1U}$ .

12.15 Yes, it is zero.

**Chapter 13**13.1 (a)  $7.73 \times 10^{-32}$  J m $^{-3}$  s; (b)  $v = 6.2 \times 10^{-28}$  J m $^{-3}$  s.13.2  $s = 6.36 \times 10^7$  m s $^{-1}$ .

13.3 (a) 1.59 ns; (b) 2.48 ps.

- 13.4** (a) 160 MHz; (b) 16 MHz.  
**13.5**  $v = 3.4754 \times 10^{11} \text{ s}^{-1}$ .  
**13.6** (a)  $I = 3.307 \times 10^{-47} \text{ kg m}^2$ ; (b)  $R = 141 \text{ pm}$ .  
**13.7** (a)  $I = 5.420 \times 10^{-46} \text{ kg m}^2$ ; (b)  $R = 162.8 \text{ pm}$ .  
**13.8**  $R = 116.21 \text{ pm}$ .

**13.9**  $R_{\text{CO}} = 116.1 \text{ pm}$ ;  $R_{\text{CS}} = 155.9 \text{ pm}$ .

**13.10**  $\bar{v}_{\text{Stokes}} = 20\ 603 \text{ cm}^{-1}$ .

**13.11**  $R = 141.78 \text{ pm}$ .

**13.12** (a)  $\text{H}_2\text{O}, C_{2v}$ ; (b)  $\text{H}_2\text{O}_2, C_2$ ; (c)  $\text{NH}_3, C_{3v}$ ; (d)  $\text{N}_2\text{O}, C_{\infty v}$ .

**13.13** (a)  $\text{CH}_2\text{Cl}_2$ ; (b)  $\text{CH}_3\text{CH}_3$ ; (d)  $\text{N}_2\text{O}$ .

**13.14**  $k = 0.71 \text{ N m}^{-1}$ .

**13.15** 28.4 per cent.

**13.16**  $k = 245.9 \text{ N m}^{-1}$ .

**13.17** (a) 0.212; (b) 0.561.

**13.18** DF:  $\bar{v} = 3002.3 \text{ cm}^{-1}$ , DCl:  $\bar{v} = 2143.7 \text{ cm}^{-1}$ , DBr:  $\bar{v} = 1885.8 \text{ cm}^{-1}$ , DI:  $\bar{v} = 1640.1 \text{ cm}^{-1}$ .

**13.19**  $\bar{v} = 2374.05 \text{ cm}^{-1}$ ,  $x_c = 6.087 \times 10^{-3}$ .

**13.20**  $D_0 = 3.235 \times 10^4 \text{ cm}^{-1} = 4.01 \text{ eV}$ .

**13.21**  $\bar{v}_R = 2347.16 \text{ cm}^{-1}$ .

**13.22** (a)  $\text{CH}_3\text{CH}_3$ ; (b)  $\text{CH}_4$ ; (c)  $\text{CH}_3\text{Cl}$ .

**13.23** (a) 30; (b) 42; (c) 13.

**13.24** (a) IR active =  $A''_2 + E'$ , Raman active =  $A_1 + E'$ ;  
(b) IR active =  $A_1 + E$ , Raman active =  $A_1 + E$ .

**13.25** (a) IR active; (b) Raman active.

**13.26**  $A_{1g} + A_{2g} + E_{1u}$ .

## Chapter 14

**14.1** multiplicity = 3, parity = u.

**14.2** 22.2 per cent.

**14.3**  $\epsilon = 7.9 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$ .

**14.4**  $1.33 \times 10^{-3} \text{ mol dm}^{-3}$ .

**14.5**  $A = 1.56 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$ .

**14.6** Rise.

**14.7**  $\epsilon = 522 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

**14.8**  $\epsilon = 128 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $T = 0.13$ .

**14.9** (a) 0.010 cm; (b) 0.033 cm.

**14.10** (a)  $1.39 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$ ; (b)  $1.39 \times 10^9 \text{ m mol}^{-1}$ .

**14.11** Stronger.

## Chapter 15

**15.1**  $v = 649 \text{ MHz}$ .

**15.2**  $E_{m_i} = -2.35 \times 10^{-26} \text{ J}$ , 0,  $+2.35 \times 10^{-26} \text{ J}$ .

**15.3** 47.3 MHz.

**15.4** (a)  $\Delta E = 2.88 \times 10^{-26} \text{ J}$ ; (b)  $\Delta E = 5.77 \times 10^{-24} \text{ J}$ .

**15.5** 3.523 T.

	B/T	$^{14}\text{N}$	$^{19}\text{F}$	$^{31}\text{P}$
	$g_I$	0.40356	5.2567	2.2634
(a)	300 MHz	97.5	7.49	17.4
(b)	750 MHz	244	18.7	43.5

**15.7** (a)  $4.3 \times 10^{-7}$ ; (b)  $2.2 \times 10^{-6}$ ; (c)  $1.34 \times 10^{-5}$ .

**15.8** (a)  $\delta$  is independent of both B and  $v$ . (b)  $\frac{v - v^\circ(800 \text{ MHz})}{v - v^\circ(60 \text{ MHz})} = 13$ .

**15.9** (a)  $4.2 \times 10^{-6} \text{ T}$ ; (b)  $3.63 \times 10^{-5} \text{ T}$ . Spectrum appears narrower at 650 MHz.

**15.11**  $2.9 \times 10^3 \text{ s}^{-1}$ .

**15.14** (a) The H and F nuclei are both chemically and magnetically equivalent. (b) The P and H nuclei chemically and magnetically equivalent in both the *cis*- and *trans*-forms.

**15.15**  $B_1 = 9.40 \times 10^{-4} \text{ T}$ ,  $6.25 \mu\text{s}$ .

**15.16** 1.3 T.

**15.17**  $g = 2.0022$ .

**15.18** 2.2 mT,  $g = 1.992$ .

**15.19** Eight equal parts at  $\pm 1.445 \pm 1.435 \pm 1.055 \text{ mT}$  from the centre, namely: 328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625 and 336.735 mT.

**15.21** (a) 332.3 mT; (b) 1209 mT.

**15.22**  $I = 1$ .

## Chapter 16

**16.1**  $T = 623 \text{ K}$ .

**16.2** (a) 15.9 pm, 5.04 pm; (b)  $2.47 \times 10^{26}$ ,  $7.82 \times 10^{27}$ .

**16.3**  $\frac{q_{\text{Xe}}}{q_{\text{He}}} = 187.9$ .

**16.4**  $q = 4.006$ .

**16.5**  $E = 7.605 \text{ kJ mol}^{-1}$ .

**16.6** 213 K.

**16.7** (a) 0.997, 0.994; (b) 0.999 99, 0.999 98.

**16.8** (a) (i)  $\frac{n_2}{n_1} = 1.39 \times 10^{-11}$ ,  $\frac{n_3}{n_1} = 1.93 \times 10^{-22}$ ;

(ii)  $\frac{n_2}{n_1} = 0.368$ ,  $\frac{n_3}{n_1} = 0.135$ ;

(iii)  $\frac{n_2}{n_1} = 0.779$ ,  $\frac{n_3}{n_1} = 0.607$ ;

(b)  $q = 1.503$ ; (c)  $U_m = 88.3 \text{ J mol}^{-1}$ ;

(d)  $C_v = 3.53 \text{ J K}^{-1} \text{ mol}^{-1}$ ; (e)  $S_m = 6.92 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**16.9** 7.26 K.

**16.10** (a)  $147 \text{ J K}^{-1} \text{ mol}^{-1}$ ; (b)  $169.6 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**16.11**  $10.7 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**16.12** (a)

## Chapter 17

**17.1** (a)  $\text{O}_3 : 3R$  [experimental =  $3.7R$ ]

(b)  $\text{C}_2\text{H}_6 : 4R$  [experimental =  $6.3R$ ]

(c)  $\text{CO}_2 : \frac{5}{3}R$  [experimental =  $4.5R$ ]

**17.2** With vibrations: 115, Without vibrations: 140, Experimental: 1.29.

**17.3** (a) 143; (b) 251.

**17.4** (a) 2; (b) 2; (c) 6; (d) 24; (e) 4.

**17.5**  $q^K = 5837$ ,  $\theta_R = 0.8479 \text{ K}$ ,  $T = 0.3335 \text{ K}$ .

**17.6**  $S_m^R = 84.57 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(a) At 298 K,  $q^R = 2.50 \times 10^3$ . At 500 K,  $q^R = 5.43 \times 10^3$ ;

(b) At 298 K,  $q = 2.50 \times 10^3$ . At 500 K,  $q = 5.43 \times 10^3$ .

**17.8** (a) At  $25^\circ\text{C}$ ,  $q^R = 7.97 \times 10^3$ ; (b) At  $100^\circ\text{C}$ ,  $q^R = 1.12 \times 10^4$ .

**17.9** (a) At 298 K,  $S_m = 5.88 \text{ J mol}^{-1} \text{ K}^{-1}$ .

(b) At 500 K,  $S_m = 16.48 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**17.10**  $G_m^R - G_m^R(0) = -20.1 \text{ kJ mol}^{-1}$ ,  $G_m^V - G_m^V(0) = -0.110 \text{ kJ mol}^{-1}$ .

**17.11**  $-3.65 \text{ kJ mol}^{-1}$ .

**17.12**  $S_m = 14.9 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**17.14**  $K \approx 0.25$ .

## Chapter 18

- 18.1** SF<sub>4</sub>.
- 18.2**  $\mu = 1.4$  D.
- 18.3**  $\mu = 9.45 \times 10^{-29}$  C m,  $\theta = 194.0^\circ$ .
- 18.4**  $\mu = 3.23 \times 10^{-30}$  C m,  $\alpha = 2.55 \times 10^{-39}$  C<sup>2</sup> m<sup>2</sup> J<sup>-1</sup>.
- 18.5**  $\varepsilon_r = 8.97$ .
- 18.6**  $\mu^* = 3.71 \times 10^{-36}$  C m.
- 18.7**  $\alpha = 3.40 \times 10^{-40}$  C<sup>2</sup> m<sup>2</sup> J<sup>-1</sup>.
- 18.8**  $n_r = 1.10$ .
- 18.9**  $\varepsilon_r = 16$ .
- 18.10**  $p = 5.92$  kPa.
- 18.11**  $\gamma = 7.12 \times 10^{-2}$  N m<sup>-1</sup>.
- 18.12**  $p_{in} - p_{out} = 2.04 \times 10^5$  Pa.

## Chapter 19

- 19.1**  $\bar{M}_n = 68$  kg mol<sup>-1</sup>,  $\bar{M}_w = 69$  kg mol<sup>-1</sup>.
- 19.2**  $R_g = 1.06 \times 10^4$ .
- 19.3** (a)  $\bar{M}_n = 8.8$  kg mol<sup>-1</sup>; (b)  $\bar{M}_w = 11$  kg mol<sup>-1</sup>.
- 19.4**  $\tau = 9.4 \times 10^{-8}$  s.
- 19.5** 71.
- 19.6**  $\bar{M}_n = 120$  kg mol<sup>-1</sup>.
- 19.7**  $s = 1.47 \times 10^{-4}$  m s<sup>-1</sup>.
- 19.8**  $\bar{M} = 56$  kg mol<sup>-1</sup>.
- 19.9**  $\bar{M}_w = 3.1 \times 10^3$  kg mol<sup>-1</sup>.
- 19.10**  $a/g = 3.86 \times 10^5$ .
- 19.11**  $R_{rms} = 38.97$  nm.
- 19.12**  $R_c = 1.26 \times 10^{-6}$  m,  $R_{rms} = 1.97 \times 10^{-8}$  m.

## Chapter 20

- 20.1**  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(0, \frac{1}{2}, \frac{1}{2})$ .
- 20.2** (3 1 3) and (6 4 3).
- 20.3**  $d_{121} = 214$  pm,  $d_{221} = 174$  pm,  $d_{244} = 87.2$  pm.
- 20.4**  $\lambda = 86.7$  pm.

20.5	hkl	sin θ	θ/°	2θ/°
	111	0.327	19.1	38.2
	200	0.378	22.2	44.4
	220	0.535	32.3	64.6

- 20.6**  $D = 0.054$  cm.
- 20.7**  $V = 1.2582$  nm<sup>3</sup>.
- 20.8**  $d = 5$ ,  $d = 2.90$  g cm<sup>-3</sup>.
- 20.9**  $d_{322} = 182$  pm.
- 20.10** (100), (110), (111), and (200).

20.11	hkl	$d_{hkl}/\text{pm}$	$\theta_{hkl}/^\circ$
	100	574.1	4.166
	010	796.8	3.000
	111	339.5	7.057

- 20.12** body-centred cubic.
- 20.13**  $F_{hkl} = 2f$  for  $h + k + l$  even; 0 for  $h + k + l$  odd.

**20.14**  $\frac{2}{3}.$

**20.15**  $\frac{r}{R} = 0.732$ .

**20.16** (a) 57 pm; (b) 111 pm.

**20.17**  $\frac{2V_{\text{atom}}}{V_{\text{cell}}} = 0.370$ .

**20.18** contraction.

**20.20**  $\lambda = 252$  pm.

**20.21**  $\Delta_l H^\ominus(\text{MgBr}_2, s) = 2421$  kJ mol<sup>-1</sup>.

**20.23** strain =  $5.8 \times 10^{-2}$ .

**20.24**  $\Delta V = 0.003$  dm<sup>3</sup>.

**20.25** p-type.

**20.26**  $2.71 \times 10^4$  H.

**20.27** 5.

**20.28**  $-8.2 \times 10^{-4}$  cm<sup>3</sup> mol<sup>-1</sup>.

**20.29**  $\chi_m = 1.58 \times 10^{-8}$  m<sup>3</sup> mol<sup>-1</sup>, dimerization occurs.

**20.30** 2.52 = effective unpaired spins, theoretical number = 2.

**20.31**  $\chi_m = 1.85 \times 10^{-7}$  m<sup>3</sup> mol<sup>-1</sup>.

**20.32**  $r = 0.935$ .

## Chapter 21

- 21.1** (a) 7.079; (b) 1.
- 21.2** (a)  $c = 4.75 \times 10^2$  m s<sup>-1</sup>; (b)  $\lambda = 4 \times 10^4$  m; (c)  $z = 0.01$  s<sup>-1</sup>.
- 21.3**  $p = 2.4 \times 10^7$  Pa.
- 21.4**  $\lambda = 4.1 \times 10^{-7}$  m.
- 21.5**  $z = 9.9 \times 10^8$  s<sup>-1</sup>.
- 21.6** (a)  $\lambda = 3.7 \times 10^{-9}$  m; (b)  $\lambda = 5.5 \times 10^{-8}$  m; (c)  $\lambda = 4.1 \times 10^{-5}$  m.
- 21.7**  $F \approx 9.6 \times 10^{-2}$ .
- 21.8**  $N = 5.3 \times 10^{21}$ .
- 21.9**  $\Delta m = 4.98 \times 10^{-4}$  kg.
- 21.10**  $M_{\text{fluorocarbon}} = 554$  g mol<sup>-1</sup>.
- 21.11**  $t = 1.5 \times 10^4$  s.
- 21.12**  $0.17$  J m<sup>-2</sup> s<sup>-1</sup>.
- 21.13**  $1.61 \times 10^{-19}$  m<sup>2</sup>.
- 21.14**  $22$  J s<sup>-1</sup>.
- 21.15**  $3.00 \times 10^{-19}$  m<sup>2</sup>.
- 21.16**  $1.00 \times 10^5$  Pa.
- 21.17** (a) At 273 K:  $\eta = 0.95 \times 10^{-5}$  kg m<sup>-1</sup> s<sup>-1</sup>;  
(b) At 298 K:  $\eta = 0.99 \times 10^{-5}$  kg m<sup>-1</sup> s<sup>-1</sup>;  
(c) At 1000 K:  $\eta = 1.81 \times 10^{-5}$  kg m<sup>-1</sup> s<sup>-1</sup>.
- 21.18** (a)  $\kappa = 0.0114$  J m<sup>-1</sup> s<sup>-1</sup> K<sup>-1</sup>,  $0.017$  J s<sup>-1</sup>;  
(b)  $\kappa = 9.0 \times 10^{-3}$  J m<sup>-1</sup> s<sup>-1</sup> K<sup>-1</sup>,  $0.014$  J s<sup>-1</sup>.
- 21.19**  $52.0 \times 10^{-7}$  kg m<sup>-1</sup> s<sup>-1</sup>,  $d = 923$  pm.
- 21.20**  $\kappa = 9.0 \times 10^{-3}$  J m<sup>-1</sup> s<sup>-1</sup> K<sup>-1</sup>.
- 21.21** (a)  $D = 0.107$  m<sup>2</sup> s<sup>-1</sup>,  $J = 0.87$  mol m<sup>-2</sup> s<sup>-1</sup>;  
(b)  $D = 1.07 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup>,  $J = 8.7 \times 10^{-5}$  mol m<sup>-2</sup> s<sup>-1</sup>;  
(c)  $D = 7.13 \times 10^{-8}$  m<sup>2</sup> s<sup>-1</sup>,  $J = 5.8 \times 10^{-7}$  mol m<sup>-2</sup> s<sup>-1</sup>.
- 21.22**  $4.09 \times 10^{-3}$  S m<sup>2</sup> mol<sup>-1</sup>.
- 21.23**  $4.81 \times 10^{-5}$  m V<sup>-1</sup> s<sup>-1</sup>.
- 21.24** 0.604.
- 21.25**  $A_m^\ominus(\text{MgI}_2) = 25.96$  mS m<sup>2</sup> mol<sup>-1</sup>.
- 21.26** F<sup>-</sup>:  $u = 5.74 \times 10^{-8}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>;  
Cl<sup>-</sup>:  $u = 7.913 \times 10^{-8}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>;  
Br<sup>-</sup>:  $u = 8.09 \times 10^{-8}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.
- 21.27**  $1.09 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>.
- 21.28**  $4.1 \times 10^3$  s.

**21.29** 207 pm.

**21.30**  $200 \times 10^{-11}$  s = 20 ps.

**21.31** Iodine: (a) 78 s; (b)  $7.8 \times 10^3$  s.

Sucrose: (a)  $3.2 \times 10^2$  s; (b)  $3.2 \times 10^4$  s.

## Chapter 22

**22.1** Rates of consumption of A =  $1.0 \text{ mol dm}^{-3} \text{ s}^{-1}$ ; B =  $3.0 \text{ mol dm}^{-3} \text{ s}^{-1}$ ; C =  $1.0 \text{ mol dm}^{-3} \text{ s}^{-1}$ ; D =  $2.0 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

**22.2** Rate of consumption of B =  $1.00 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

Rate of reaction =  $0.33 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

Rate of formation of C =  $0.33 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

Rate of formation of D =  $0.66 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

Rate of consumption of A =  $0.33 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

**22.3** K:  $\text{dm}^3 \text{ mol}^{-2} \text{ s}^{-1}$ . (a)  $v = \frac{d[A]}{dt} = -k[A][B]^2$ ; (b)  $v = \frac{d[C]}{dt} = k[A][B]^2$ .

**22.4**  $v = k[A][B][C]^{-1}$ , K:  $\text{s}^{-1}$ .

**22.5** 2.00.

**22.6** Reaction order = 0.

**22.7**  $t_{1/2} = 1.80 \times 10^6$  s, (a)  $p = 31.5 \text{ kPa}$ ; (b)  $p = 29.0 \text{ kPa}$ .

**22.8** (a)  $k = 3.47 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ; (b)  $t_{1/2}(A) = 2.4 \text{ h}$ ;  $t_{1/2}(B) = 0.44 \text{ h}$ .

**22.9** (a) Second-order units:  $\text{m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , Third-order units:  $\text{m}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ; (b) Second-order units;  $\text{Pa}^{-1} \text{ s}^{-1}$ , Third-order units;  $\text{Pa}^{-2} \text{ s}^{-1}$ .

**22.10** (a)  $6.5 \times 10^{-3} \text{ mol dm}^{-3}$ ; (b)  $0.025 \text{ mol dm}^{-3}$ .

**22.11**  $1.5 \times 10^6$  s.

**22.12**  $t_{1/3} = \frac{3^{n-1} - 1}{k(n-1)} [A]_0^{1-n}$ .

**22.13**  $K_f = 1.7 \times 10^{-7} \text{ s}^{-1}$ ,  $k_r = 8.3 \times 10^8 \text{ dm mol}^{-1} \text{ s}^{-1}$ .

**22.14**  $E_a = 9.9 \text{ kJ mol}^{-1}$ , A =  $0.94 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

**22.15** (a)  $k_T/k_H \approx 0.06$ ; (b)  $k_{18}/k_{16} \approx 0.89$ .

**22.16**  $k_a = 9.9 \times 10^{-6} \text{ s}^{-1} \text{ Pa}^{-1} = 9.9 \text{ s}^{-1} \text{ MPa}^{-1}$ .

## Chapter 23

**23.2**  $\frac{d[R_2]}{dt} = -k_1[R_2] - k_2 \left( \frac{k_1}{k_4} \right)^{1/2} [R_2]^{3/2}$ .

**23.3** (a) Does not occur. (b)  $p = 1.3 \times 10^2 \text{ Pa}$  to  $3 \times 10^4 \text{ Pa}$ .

**23.4**  $\frac{k_1 k_2 K_a^{1/2}}{k'_1} [HA]^{3/2} [B]$ .

**23.5**  $\frac{d[A_2]}{dt} = -k_1[A_2]$ .

**23.6**  $v_{\max} = 2.57 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ .

**23.7**  $1.5 \times 10^{-5}$  moles of photons.

**23.8**  $\Phi = 1.11$ .

## Chapter 24

**24.1**  $z = 6.64 \times 10^9 \text{ s}^{-1}$ ,  $Z_{AA} = 8.07 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}$ , 1.6 per cent.

**24.2** (a) (i)  $2.4 \times 10^{-3}$ , (ii) 0.10; (b) (i)  $7.7 \times 10^{-27}$ , (ii)  $1.6 \times 10^{-10}$ .

**24.3** (a) (i) 1.2, (ii) 1.03; (b) (i) 7.4, (ii) 1.3.

**24.4**  $k = 1.7 \times 10^{-12} \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ .

**24.5**  $k_d = 3.2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  or  $3.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

**24.6** (a)  $k_d = 1.97 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ; (b)  $k_d = 2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

**24.7**  $k_d = 1.10 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  or  $1.10 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,

$t_{1/2} = 5.05 \times 10^{-8} \text{ s}$ .

**24.8**  $P = 1.41 \times 10^{-3}$ .

**24.9**  $v = 1.54 \times 10^8 \text{ mol dm}^{-3} \text{ s}^{-1}$ .

**24.10**  $\Delta^\ddagger H = 48.52 \text{ kJ mol}^{-1}$ ,  $\Delta^\ddagger S = -32.2 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**24.11**  $\Delta^\ddagger G = 46.8 \text{ kJ mol}^{-1}$ .

**24.12**  $\Delta^\ddagger S = -93 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**24.13**  $\Delta^\ddagger S = -80.0 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**24.14** (a)  $\Delta^\ddagger S = -24.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ; (b)  $\Delta^\ddagger H = 27.5 \text{ kJ mol}^{-1}$ ;

(c)  $\Delta^\ddagger G = 34.7 \text{ kJ mol}^{-1}$ .

**24.15**  $k_2 = 1.08 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$ .

**24.16**  $\lambda = 1.531 \text{ eV}$ ,  $\langle H_{DA} \rangle = 9.39 \times 10^{-24} \text{ J}$ .

**24.17**  $k_{et} = 1.4 \times 10^3 \text{ s}^{-1}$ .

## Chapter 25

**25.1** (a) (i)  $2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ , (ii)  $5.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ ;

(b) (i)  $3.81 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ , (ii)  $7.60 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ .

**25.2**  $p = 7.3 \times 10^2 \text{ Pa}$ .

**25.3**  $6.6 \times 10^4 \text{ s}^{-1}$ .

**25.4**  $A = 18.8 \text{ m}^2$ .

**25.5**  $V_{\text{mon}} = 9.7 \text{ cm}^3$ .

**25.6**  $t_{1/2} = 200 \text{ s}$ .

**25.7**  $E_d = 3.7 \times 10^3 \text{ J mol}^{-1}$ .

**25.8** (a) 0.32 kPa; (b) 3.9 kPa.

**25.9**  $\theta_1 = 0.75$ ,  $\theta_2 = 0.25$ .

**25.10** (a) At 400 K:  $4.9 \times 10^{-11} \text{ s}$ , At 800 K:  $2.4 \times 10^{-12} \text{ s}$ ;

(b) At 400 K:  $1.6 \times 10^{13} \text{ s}$ , At 800 K: 1.4 s.

**25.11**  $p_2 = 6.50 \text{ kPa}$ .

**25.12** (a)  $\theta = \frac{K_p}{1 + K_p}$ ; (b)  $\theta = \frac{(K_p)^{1/2}}{1 + (K_p)^{1/2}}$ ;

(c)  $\theta = \frac{(K_p)^{1/3}}{1 + (K_p)^{1/3}}$ . A plot of  $\theta$

versus  $p$  at low pressures (where the denominator is approximately 1) would show progressively weaker dependence on  $p$  for dissociation into two or three fragments.

**25.13**  $\Delta_{\text{aq}} H^\ddagger = -6.40 \text{ kJ mol}^{-1}$ .

**25.14**  $E_d = 2.85 \times 10^5 \text{ J mol}^{-1}$ . (a)  $t = 1.48 \times 10^{36} \text{ s}$ ; (b)  $t = 1.38 \times 10^{-4} \text{ s}$ .

**25.15**  $\varepsilon = 2.8 \times 10^8 \text{ V m}^{-1}$ .

**25.16** 167 mV.

**25.17**  $j_0 = 1.6 \text{ mA cm}^{-2}$ .

**25.18**  $j_2 = 8.5 \text{ mA cm}^{-2}$ .

**25.19** (a)  $j = 0.34 \text{ A cm}^{-2}$ ;  
(b)  $j = 0.34 \text{ A cm}^{-2}$ . The validity of the Tafel equation improves as the overpotential increases.

**25.20**  $j_{\text{lim}} = 1.3 \text{ A m}^{-2}$ .

**25.21**  $[Fe^{2+}] = 4 \times 10^{-6} \text{ mol dm}^{-3}$ .

**25.22**  $j = (2.5 \text{ mA cm}^{-2}) \times [(e^{(0.42)E'/f} \times (3.41 \times 10^{-6}) - e^{(-0.58)E'/f} \times (3.55 \times 10^7)]$ .

**25.23** At  $r = 0.1$ :  $j/j_0 = 1.5 \text{ A cm}^{-2}$ ,

At  $r = 1$ :  $j/j_0 = 4.8 \text{ A cm}^{-2}$ ,

At  $r = 10$ :  $j/j_0 = 15 \text{ A cm}^{-2}$ .

**25.24** 0.61 V.

**25.25** For the Cu,  $H_2|H^+$  electrode:  $N = 6.2 \times 10^{12} \text{ s}^{-1} \text{ cm}^{-2}$ ,  $f = 4.2 \times 10^{-3} \text{ s}^{-1}$ .

For the Pt| $Ce^{4+}, Ce^{3+}$  electrode:  $N = 2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}$ ,  $f = 0.17 \text{ s}^{-1}$ .

**25.26** (a) 5.1 GΩ; (b) 10 GΩ.

**25.29** Deposition would not occur.

**25.30** Iron can be deposited.

**25.31**  $E^\ddagger = 1.80 \text{ V}$ ,  $P = 0.180 \text{ W}$ .

**25.32** 3.0 mm  $y^{-1}$ .

# Solutions to odd problems

## Chapter 1

- 1.1**  $-233^\circ\text{N}$ .
- 1.3**  $-272.95^\circ\text{C}$ .
- 1.5** (a)  $\Delta p = 0.0245 \text{ kPa}$ ; (b)  $p = 9.14 \text{ kPa}$ ; (c)  $\Delta p = 0.0245 \text{ kPa}$ .
- 1.7** (a)  $V_m = 12.5 \text{ dm}^3 \text{ mol}^{-1}$ ; (b)  $V_m = 12.3 \text{ dm}^3 \text{ mol}^{-1}$ .
- 1.9** (a)  $0.944 \text{ dm}^3 \text{ mol}^{-1}$ ;  
 (b)  $2.69 \text{ dm}^3 \text{ mol}^{-1}$ ,  $2.67 \text{ dm}^3 \text{ mol}^{-1}$ ;  
 (c)  $5.11 \text{ dm}^3 \text{ mol}^{-1}$
- 1.11** (a)  $0.1353 \text{ dm}^3 \text{ mol}^{-1}$ ; (b)  $0.6957$ ; (c)  $0.72$ .
- 1.13**  $b = 59.4 \text{ cm}^3 \text{ mol}^{-1}$ ,  $a = 5.649 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $p = 21 \text{ atm}$ .
- 1.15**  $B = b - \frac{a}{RT}$ ,  $C = b^2$ ,  $b = 34.6 \text{ cm}^3 \text{ mol}^{-1}$ ,  $a = 1.26 \text{ dm}^6 \text{ atm mol}^{-2}$ .
- 1.17**  $V_c = \frac{3C}{B}$ ,  $T_c = \frac{B^2}{3RC}$ ,  $p_c = \frac{B^3}{27C^2}$ ,  $Z_c = \frac{1}{3}$
- 1.19**  $B' = 0.082 \text{ atm}^{-1}$ ,  $B = 2.0 \text{ dm}^3 \text{ mol}^{-1}$ .
- 1.21** No.
- 1.23** 0.011.
- 1.25**  $4.1 \times 10^8 \text{ dm}^3$
- 1.27** (a) 0.00; (b)  $-0.72$
- 1.31**  $h = 51.5 \text{ km}$ .  
 $p = 3.0 \times 10^{-3} \text{ bar}$ .

## Chapter 2

- 2.1**  $T_1 = 273 \text{ K} = T_3$ ,  $T_2 = 546 \text{ K}$   
 Step 1  $\rightarrow$  2:  $w = -2.27 \times 10^3 \text{ J}$   
 $\Delta U = +3.40 \times 10^3 \text{ J}$   
 $q = +5.67 \times 10^3 \text{ J}$   
 $\Delta H = +5.67 \times 10^3 \text{ J}$
- Step 2  $\rightarrow$  3:  $w = 0$   
 $q_v = \Delta U = -3.40 \times 10^3 \text{ J}$   
 $\Delta H = -5.67 \times 10^3 \text{ J}$
- Step 3  $\rightarrow$  1:  $\Delta U = \Delta H = 0$   
 $-q = w = +1.57 \times 10^3 \text{ J}$
- Cycle:  $\Delta U = \Delta H = 0$   
 $q = -w = +0.70 \times 10^3 \text{ J}$
- 2.3**  $w = 0$ ,  $\Delta U = +2.35 \text{ kJ}$ ,  $\Delta H = +3.03 \text{ kJ}$ ,
- 2.5** (a)  $w = 0$ ,  $\Delta U = +6.19 \text{ kJ}$ ,  $q = +6.19 \text{ kJ}$ ,  $\Delta H = +8.67 \text{ kJ}$ ;  
 (b)  $q = 0$ ,  $\Delta U = -6.19 \text{ kJ}$ ,  $\Delta H = -8.67 \text{ kJ}$ ,  $w = -6.19 \text{ kJ}$ ;  
 (c)  $\Delta U = \Delta H = 0$ ,  $-q = w = +4.29 \text{ kJ}$ .  
 (a)  $w_0 = -1.7 \text{ kJ}$ ; (b)  $w = -1.8 \text{ kJ}$ ; (c)  $w = -1.5 \text{ kJ}$ .
- 2.7**  $-87.33 \text{ kJ mol}^{-1}$ .
- 2.9**  $\Delta_f H^\circ = +17.7 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{metallocene}, 583 \text{ K}) = +116.0 \text{ kJ mol}^{-1}$ .
- 2.11** (c)  $n = 0.903$ ,  $k = -73.7 \text{ kJ mol}^{-1}$ .
- 2.13**  $\Delta_c H^\circ = 25\ 968 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(C_{60}) = 2357 \text{ kJ mol}^{-1}$ .
- 2.15** (a)  $240 \text{ kJ mol}^{-1}$ ; (b)  $228 \text{ kJ mol}^{-1}$ .
- 2.17**  $41.40 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- 2.19** 3.60 kJ.
- 2.21** (a)  $dz = (2x - 2y + 2)dx + (4y - 2x - 4)dy$   
 (c)  $dz = \left(y + \frac{1}{x}\right)dx + (x - 1)dy$

- 2.25** (a)  $\left(\frac{\partial H}{\partial U}\right)_p = 1 + p\left(\frac{\partial V}{\partial U}\right)_p = 1 + \frac{p}{(\partial U/\partial V)_p}$   
 (b)  $\left(\frac{\partial H}{\partial U}\right)_p = 1 + \frac{p}{(\partial U/\partial V)_p} = 1 + p\left(\frac{\partial V}{\partial U}\right)_p$
- 2.27** (a)  $-1.5 \text{ kJ}$ , (b)  $-1.6 \text{ kJ}$ .
- 2.29** increase.
- 2.37** (a)  $\mu = \frac{aT^2}{C_p}$   
 (b)  $C_v = C_p - R\left(1 + \frac{2apT}{R}\right)^2$
- 2.39** 7.4%.
- 2.41** (a)  $-25 \text{ kJ}$ ; (b)  $9.7 \text{ m}$ ; (c)  $39 \text{ kJ}$ ; (d)  $15 \text{ m}$ .
- 2.45**  $\Delta T = 2^\circ\text{C}$ ,  $\Delta h = 1.6 \text{ m}$ ,  $\Delta T = 1^\circ\text{C}$ ,  $\Delta h = 0.8 \text{ m}$ ,  $\Delta T = 3.5^\circ\text{C}$ ,  $\Delta h = 2.8 \text{ m}$ .
- 2.47** (a)  $23.5 \text{ K MPa}^{-1}$ ; (b)  $14.0 \text{ K MPa}^{-1}$ .

## Chapter 3

- 3.1** (a)  $\Delta_{\text{trs}} S(l \rightarrow s, -5^\circ\text{C}) = -21.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta S_{\text{sur}} = +21.7 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta S_{\text{total}} = +0.4 \text{ J K}^{-1} \text{ mol}^{-1}$ .  
 (b)  $\Delta_{\text{trs}} S(l \rightarrow g, T) = +109.7 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta S_{\text{sur}} = -111.2 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta S_{\text{total}} = -1.5 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- 3.3** (a)  $q(\text{Cu}) = 43.9 \text{ kJ}$ ,  $q(\text{H}_2\text{O}) = -43.9 \text{ kJ}$ ,  $\Delta S(\text{H}_2\text{O}) = -118.1 \text{ J K}^{-1}$ ,  $\Delta S(\text{Cu}) = 145.9 \text{ J K}^{-1}$ ,  $\Delta S(\text{total}) = 28 \text{ J K}^{-1}$ .  
 (b)  $\theta = 49.9^\circ\text{C} = 323.1 \text{ K}$ ,  $q(\text{Cu}) = 38.4 \text{ kJ} = -q(\text{H}_2\text{O})$ ,  $\Delta S(\text{H}_2\text{O}) = -119.8 \text{ J K}^{-1}$ ,  $\Delta S(\text{Cu}) = 129.2 \text{ J K}^{-1}$ ,  $\Delta S(\text{total}) = 9 \text{ J K}^{-1}$ .

	Step 1	Step 2	Step 3	Step 4	Cycle
$q$	+11.5 kJ	0	-5.74 kJ	0	-5.8 kJ
$w$	-11.5 kJ	-3.74 kJ	+5.74 kJ	+3.74 kJ	-5.8 kJ
$\Delta U$	0	-3.74 kJ	0	+3.74 kJ	0
$\Delta H$	0	-6.23 kJ	0	+6.23 kJ	0
$\Delta S$	+19.1 J K <sup>-1</sup>	0	-19.1 J K <sup>-1</sup>	0	0
$\Delta S_{\text{tot}}$	0	0	0	0	0
$\Delta G$	-11.5 kJ	Indeterminate	+11.5 kJ	Indeterminate	0

- 3.7** (a)  $200.7 \text{ J K}^{-1} \text{ mol}^{-1}$ ; (b)  $232.0 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- 3.9**  $\Delta S = nC_{p,m} \ln \frac{T_f}{T_h} + nC_{p,m} \ln \frac{T_f}{T_c}$ ,  $\Delta S = +22.6 \text{ J K}^{-1}$ .
- 3.11** (a)  $63.88 \text{ J K}^{-1} \text{ mol}^{-1}$ ; (b)  $66.08 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- 3.13**  $H_m^\circ(200 \text{ K}) - H_m^\circ(0) = 32.1 \text{ kJ mol}^{-1}$ .
- 3.15**  $46.60 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- 3.17** (a)  $-7 \text{ kJ mol}^{-1}$ ; (b)  $+107 \text{ kJ mol}^{-1}$ .
- 3.29**  $\pi_T \approx \frac{p^2}{R} \times \frac{\Delta B}{\Delta T}$   
 (a)  $3.0 \times 10^{-3} \text{ atm}$ ; (b)  $0.30 \text{ atm}$ .
- 3.31**  $\pi_T = \frac{nap}{RTV}$
- 3.33**  $T dS = C_p dT - \alpha TV dp$ ,  $q_{\text{rev}} = -\alpha TV \Delta p$ ,  $q_{\text{rev}} = -0.50 \text{ kJ}$

**3.35**  $\ln \phi = \frac{Bp}{RT} + \frac{(C - B^2)p^2}{2R^2T^2} + \dots$

$f = 0.9991$  atm

-21 kJ mol<sup>-1</sup>.

**3.39** 13 per cent increase.

**3.43**  $\varepsilon = 1 - \left( \frac{V_B}{V_A} \right)^{1/c}$

$\varepsilon = 0.47$

$\Delta S_1 = \Delta S_3 = \Delta S_{\text{sur},1} = \Delta S_{\text{sur},2} = \boxed{0}$  [adiabatic reversible steps]

$\Delta S_2 = \Delta S_{\text{sur},4} = +33 \text{ J K}^{-1} = -\Delta S_{\text{sur},2} = -\Delta S_4$

**3.45** (a) 1.00 kJ; (b) 8.4 kJ.

## Chapter 4

**4.1** 196.0 K, 11.1 Torr.

**4.3** (a) 5.56 kPa K<sup>-1</sup>; (b) 2.5 per cent.

**4.5** (a) -1.63 cm<sup>3</sup> mol<sup>-1</sup>; (b) +30.1 dm<sup>3</sup> mol<sup>-1</sup>, +0.6 kJ mol<sup>-1</sup>.

**4.7** 22°C.

**4.9** (a)  $T_b = 227.5^\circ\text{C}$ ; (b)  $\Delta_{\text{vap}}H = +53 \text{ kJ mol}^{-1}$ .

**4.11** (b) 171.18 K; (c)  $T = 383.6 \text{ K}$ ; (d) 33.0 kJ mol<sup>-1</sup>.

**4.15** 9.8 Torr.

**4.17**  $-\frac{1}{T} \times C_{p,m}$ .

**4.21** (a)  $\Delta U_r(T_r, V_r) = - \int_{T_r, \text{constant}}^{\infty} \frac{2p_r(T_r, V_r)}{T_r V_r} dV_r$ ; (c) 0.85 to 0.90.

**4.23**  $\Delta_{\text{vap}}H = 1.60 \times 10^4 \text{ bar}$ .

## Chapter 5

**5.1**  $k_A = 15.58 \text{ kPa}$ ,  $k_B = 47.03 \text{ kPa}$ .

**5.3**  $V_{\text{salt}} = -1.4 \text{ cm}^3 \text{ mol}^{-1}$ ,  $V_{\text{H}_2\text{O}} = 18.04 \text{ cm}^3 \text{ mol}^{-1}$ .

**5.5**  $V_E = 57.9 \text{ cm}^3$ ,  $V_W = 45.8 \text{ cm}^3$ ,  $\Delta V = +0.96 \text{ cm}^3$ .

**5.7** 4 ions.

**5.11** (a) propionic acid:  $V_1 = V_{\text{m},1} + a_0 x_2^2 + a_1 (3x_1 - x_2)x_2^2$ ,

oxane:  $V_2 = V_{\text{m},2} + a_0 x_1^2 + a_1 (x_1 - 3x_2)x_1^2$ ,

(b)  $V_1 = 75.63 \text{ cm}^3 \text{ mol}^{-1}$ ,  $V_2 = 99.06 \text{ cm}^3 \text{ mol}^{-1}$ .

**5.13**  $K_H = 371 \text{ bar}$ ,  $\gamma_{\text{CO}_2} = 1.01$  (at 10p/bar), 0.99 (at 20p/bar), 1.00 (at 30p/bar), 0.99 (at 40p/bar), 0.98 (at 60p/bar), 0.94 (at 80p/bar).

**5.15**  $\Delta_{\text{mix}}G = -4.6 \text{ kJ}$ .

**5.17**  $\mu_A = \mu_A^* + RT \ln x_A + gRTx_B^2$

**5.19** 80.36 cm<sup>3</sup> mol<sup>-1</sup>.

**5.25**  $p_{\text{N}_2}$  at 4.0 atm = 56 µg,  $p_{\text{N}_2}$  at 1.0 atm = 14 µg, increase =  $1.7 \times 10^2 \text{ µg N}_2$ .

**5.29** (a) g cm<sup>-1</sup> mol<sup>-1</sup>,

(b)  $M = 1.1 \times 10^5 \text{ g mol}^{-1}$ ,

(d)  $B' = 21.4 \text{ cm}^3 \text{ g}^{-1}$ ,  $C' = 211 \text{ cm}^6 \text{ g}^{-2}$ ,

(e)  $B' = 28.0 \text{ cm}^3 \text{ g}^{-1}$ ,  $C' = 196 \text{ cm}^6 \text{ g}^{-2}$ .

## Chapter 6

**6.1** (b) 391.0 K; (c)  $\frac{n_{\text{liq}}}{n_{\text{vap}}} = 0.532$ .

**6.3** Temperature ( $\gamma_{\text{O}_2}$ ): 0.877 (78 K), 1.079 (80 K), 1.039 (82 K), 0.995 (84 K), 0.993 (86 K), 0.990 (88 K), 0.987 (90.2 K).

**6.7** MgCu<sub>2</sub>: 16 per cent mg by mass, Mg<sub>2</sub>Cu: 43 per cent mg by mass.

**6.9** (a) Eutectic: 40.2 at per cent Si at 1268°C; 69.4 at per cent Si at 1030°C. Congruent melting compounds: Ca<sub>2</sub>Si = 1314°C; CaSi = 1324°C. Incongruent melting compounds: CaSi<sub>2</sub> = 1040°C;

- (b) At 1000°C, the phases at equilibrium will be Ca(s) and liquid (13 at per cent Si). Relative amounts,  $n_{\text{Ca}}/n_{\text{liq}} = 2.86$ ;  
(c) (i)  $n_{\text{Si}}/n_{\text{liq}} = 0.53$  at slightly above 1030°C, (ii)  $n_{\text{Si}}/n_{\text{CaSi}_2} = 0.665$  slightly below 1030°C.

**6.13** (i) Below a denaturant concentration of 0.1 only the native and unfolded forms are stable.

**6.19** (a) 2150°C (b)  $y(\text{MgO}) = 0.18$ ,  $x(\text{MgO}) = 0.35$ , (c)  $c = 2640^\circ\text{C}$ .

**6.21** (b)  $n_{\text{liq}}/n_{\text{vap}} = 10.85$ .

## Chapter 7

**7.1** (a)  $\Delta_f G^\circ = +4.48 \text{ kJ mol}^{-1}$ ; (b)  $p_{\text{IBr}} = 0.101 \text{ atm}$ .

**7.3**  $\Delta_f H^\circ = 8.48 \text{ R}$ .

**7.5**  $\Delta_f G^\circ(T)/(k \text{ mol}^{-1}) = 78 - 0.161 \times (T/\text{K})$ .

**7.7** First experiment,  $K = 0.740$ , second experiment,  $K = 5.71$ , enthalpy of dimerization = -103 kJ mol<sup>-1</sup>.

**7.9**  $\Delta H^\circ = +158 \text{ kJ mol}^{-1}$ .

**7.11** (a) At 298 K:  $1.2 \times 10^8$ ; (b) At 700 K:  $2.7 \times 10^3$ .

**7.13** (a) CuSO<sub>4</sub>:  $4.0 \times 10^{-3}$ ; ZnSO<sub>4</sub>:  $1.2 \times 10^{-2}$ ; (b)  $\gamma_{\pm}(\text{CuSO}_4) = 0.74$ ,  $\gamma_{\pm}(\text{ZnSO}_4) = 0.60$ ; (c)  $Q = 5.9$ ; (d)  $E^\circ = +1.102 \text{ V}$ ; (e)  $E = +1.079 \text{ V}$ .

**7.15** pH = 2.0.

**7.17**  $E^\circ = +0.268 \text{ V}$ ,  $\gamma_{\pm} = 0.9659$  (1.6077 mmol kg<sup>-1</sup>), 0.9509 (3.0769 mmol kg<sup>-1</sup>), 0.9367 (5.0403 mmol kg<sup>-1</sup>), 0.9232 (7.6938 mmol kg<sup>-1</sup>), 0.9094 (10.9474 mmol kg<sup>-1</sup>),

**7.19**  $\gamma = 0.533$ .

**7.21** (a)  $\left( \frac{\partial E}{\partial p} \right)_{T,n} = -\frac{\Delta_f V}{vF}$ ;

(b)  $2.80 \times 10^{-3} \text{ mV atm}^{-1}$ ;

(c) the linear fit and constancy of  $\left( \frac{\partial E}{\partial p} \right)$  are very good;

(d)  $3.2 \times 10^{-7} \text{ atm}^{-1}$ .

**7.23** -1.15 V.

**7.25**  $\xi = 1 - \left( \frac{1}{1 + ap/p^\circ} \right)^{1/2}$

**7.31** Yes.

**7.33** (b) +0.206 V.

**7.35** (iv) HNO<sub>3</sub>·3H<sub>2</sub>O is most stable.

## Chapter 8

**8.1** (a)  $\Delta E = 1.6 \times 10^{33} \text{ J m}^{-3}$ ; (b)  $\Delta E = 2.5 \times 10^{-4} \text{ J m}^{-3}$ .

**8.3** (a)  $\theta_E = 2231 \text{ K}$ ,  $\frac{C_V}{3R} = 0.031$ ; (b)  $\theta_E = 343 \text{ K}$ ,  $\frac{C_V}{3R} = 0.897$ .

**8.5** (a)  $9.0 \times 10^{-6}$ ; (b)  $1.2 \times 10^{-6}$ .

**8.13** (a)  $N = \left( \frac{2}{L} \right)^{1/2}$ ; (b)  $N = \frac{1}{c(2L)^{1/2}}$ ; (c)  $N = \frac{1}{(\pi a^3)^{1/2}}$ ; (d)  $N = \frac{1}{(32\pi a^5)^{1/2}}$ .

**8.15** (a) Yes, eigenvalue =  $ik$ ; (b) No; (c) Yes, eigenvalue = 0; (d) No; (e) No.

**8.17** (a) Yes, eigenvalue =  $-k^2$ ;

(b) Yes, eigenvalue =  $-k^2$ ;

(c) Yes, eigenvalue = 0;

(d) Yes, eigenvalue = 0;

(e) No.

Hence, (a,b,c,d) are eigenfunctions of  $\frac{d^2}{dx^2}$ ; (b,d) are eigenfunctions

of  $\frac{d^2}{dx^2}$ , but not of  $\frac{d}{dx}$ .

8.19  $\frac{\hbar^2 k^2}{2m}$ .

8.21 (a)  $r = 6a_0$ ,  $r^2 = 42a_0^2$ ; (b)  $r = 5a_0$ ,  $r^2 = 30a_0^2$ .

8.27 (a)  $\lambda_{\text{relativistic}} = 5.35 \text{ pm}$ .

- 8.29 (a) Methane is unstable above 825 K; (b)  $\lambda_{\text{max}}$  (1000 K) = 2880 nm;  
 (c) Excitance ratio =  $7.7 \times 10^{-4}$ ; Energy density ratio =  $8.8 \times 10^{-3}$ ;  
 (d)  $2.31 \times 10^{-7}$ , it hardly shines.

## Chapter 9

9.1  $E_2 - E_1 = 1.24 \times 10^{-39} \text{ J}$ ,  $n = 2.2 \times 10^9 \text{ J}$ ,  $E_n - E_{n-1} = 1.8 \times 10^{-30} \text{ J}$ .

9.3  $E_1 = 1.30 \times 10^{-22} \text{ J}$ , minimum angular momentum =  $\pm \eta$ .

9.5 (a)  $E_1^{(1)} = \frac{ea}{L} + \frac{\epsilon}{\pi} \sin\left(\frac{\pi a}{L}\right)$ ; (b)  $E_1^{(1)} = \frac{\epsilon}{10} + \frac{\epsilon}{\pi} \sin\left(\frac{\pi}{10}\right) = 0.1984\epsilon$ .

9.11 (a)  $P = \frac{N^2}{2\kappa}$ ; (b)  $\langle x \rangle = \frac{N^2}{4\kappa^2}$ .

9.13  $\langle T \rangle = \frac{1}{2} \left( v + \frac{1}{2} \right) \hbar \omega$ .

9.15 (a)  $\delta x = L \left( \frac{1}{12} - \frac{1}{2\pi^2 n^2} \right)^{1/2}$ ,  $\delta p = \frac{n\hbar}{2L}$ ;

(b)  $\delta x = \left[ \left( v + \frac{1}{2} \right) \frac{\hbar}{\omega m} \right]^{1/2}$ ,  $\delta p = \left[ \left( v + \frac{1}{2} \right) \hbar \omega m \right]^{1/2}$ .

9.19  $\langle T \rangle = -\frac{1}{2} \langle V \rangle$ .

9.23 (a)  $E = 0$ , angular momentum = 0; (b)  $E = \frac{3\hbar^2}{I}$ , angular momentum =  $6^{1/2}\hbar$ ; (c)  $E = \frac{6\hbar^2}{I}$ , angular momentum =  $2\sqrt{3}\hbar$ .

9.25  $\theta = \arccos \frac{m_l}{\{l(l+1)\}^{1/2}}$ ,  $54^\circ 44'$ .

9.31 (a)  $\Delta E = 3.3 \times 10^{-19} \text{ J}$ ; (b)  $v = 4.95 \times 10^{-14} \text{ J s}^{-1}$ ; (c) lower, increases.

9.33  $\omega = 2.68 \times 10^{-14} \text{ J s}^{-1}$ .

9.35 (a)  $l_z = 5.275 \times 10^{-34} \text{ J s}$ ,  $E_{\pm 5} = 1.39 \times 10^{-24} \text{ J}$ ; (b)  $v = 9.2 \times 10^8 \text{ Hz}$ .

9.37  $F = 5.8 \times 10^{-11} \text{ N}$ .

## Chapter 10

10.1  $n_2 \rightarrow 6$ , transitions occur at 12 372 nm, 7503 nm, 5908 nm, 5129 nm, ..., 3908 nm (at  $n_2 = 15$ ), converging to 3282 nm as  $n_2 \rightarrow \infty$ .

10.3  $R_{\text{Li}^3} = 987\ 663 \text{ cm}^{-1}$ , the Balmer transitions lie at  $\tilde{\nu} = 137\ 175 \text{ cm}^{-1}$ , 85 187 cm<sup>-1</sup>, 122.5 eV.

10.5  ${}^2\text{P}_{1/2}$  and  ${}^2\text{P}_{3/2}$ , of which the former has the lower energy,  ${}^2\text{P}_{3/2}$  and  ${}^2\text{P}_{5/2}$  of which the former has the lower energy, the ground state will be  ${}^2\text{P}_{3/2}$ .

10.7  $3.3429 \times 10^{-24} \text{ kg}$ ,  $\frac{I_D}{I_H} = 1.000\ 272$ .

10.9 (a)  $\Delta \tilde{\nu} = 0.9 \text{ cm}^{-1}$ , (b) Normal Zeeman splitting is small compared to the difference in energy of the states involved in the transition.

10.11  $\pm 106 \text{ pm}$ .

10.13 (b) For  $3s$ ,  $\rho_{\text{node}} = 3 + \sqrt{3}$  and  $\rho_{\text{node}} = 3 - \sqrt{3}$ , no nodal plane; for  $3p_x$ ,  $\rho_{\text{node}} = 0$  and  $\rho_{\text{node}} = 4$ ,  $yz$  nodal plane ( $\phi = 90^\circ$ ); for  $3d_{xy}$ ,  $\rho_{\text{node}} = 0$ ,  $xz$  nodal plane ( $\phi = 0$ ) and  $yz$  nodal plane ( $\phi = 90^\circ$ ); (c)  $\langle r \rangle_{3s} = \frac{27a_0}{2}$ .

10.17  $\langle r^{-1} \rangle_{1s} = \frac{Z}{a_0}$ ; (b)  $\langle r^{-1} \rangle_{2s} = \frac{Z}{4a_0}$ ; (c)  $\langle r^{-1} \rangle_{2p} = \frac{Z}{4a_0}$ .

10.25 The wavenumbers for  $n = 3 \rightarrow n = 2$ :  ${}^4\text{He} = 60\ 957.4 \text{ cm}^{-1}$ ,  ${}^3\text{He} = 60\ 954.7 \text{ cm}^{-1}$ . The wavenumbers for  $n = 2 \rightarrow n = 1$ :  ${}^4\text{He} = 329\ 170 \text{ cm}^{-1}$ ,  ${}^3\text{He} = 329\ 155 \text{ cm}^{-1}$ .

10.27 (a) receding;  $s = 3.381 \times 10^5 \text{ ms}^{-1}$ .

## Chapter 11

11.3  $R = 2.1a_0$ .

- 11.7 (a)  $P = 8.6 \times 10^{-7} / P = 2.0 \times 10^{-6}$ ;  
 (b)  $P = 8.6 \times 10^{-7} / P = 2.0 \times 10^{-6}$ ;  
 (c)  $P = 3.7 \times 10^{-7} / P = 0$ ;  
 (d)  $P = 4.9 \times 10^{-7} / P = 5.5 \times 10^{-7}$ .

11.13 Delocalization energy =  $2\{E_{\text{with resonance}} - E_{\text{without resonance}}\} = \{(\alpha_O - \alpha_N)^2 + 12\beta^2\}^{1/2} - \{(\alpha_O - \alpha_N)^2 + 4\beta^2\}^{1/2}$

11.15 (a)  $\text{C}_2\text{H}_4$ : -3.813,  $\text{C}_4\text{H}_6$ : -4.623,  $\text{C}_6\text{H}_8$ : -5.538,  $\text{C}_8\text{H}_{10}$ : -5.873;  
 (b) 8.913 eV.

11.29 (a) linear relationship; (b)  $E^\bullet = -0.122 \text{ V}$ ; (c)  $E^\bullet = -0.174 \text{ V}$ , ubiquinone a better oxidizing agent than plastiquinone.

## Chapter 12

12.1 (a)  $D_{3d}$ ; (b) chair:  $D_{3d}$  boat:  $\text{C}_{2v}$ ; (c)  $D_{2h}$ ; (d)  $D_3$ ; (d)  $D_{4d}$ ; (i) Polar: Boat  $\text{C}_6\text{H}_{12}$ ; (ii) Chiral:  $[\text{Co}(\text{en})_3]^{3+}$ .

12.3  $C_2\sigma_h = i$ .

	1	$\sigma_x$	$\sigma_y$	$\sigma_z$
1	1	$\sigma_x$	$\sigma_y$	$\sigma_z$
$\sigma_x$	$\sigma_x$	1	$i\sigma_x$	$-i\sigma_y$
$\sigma_y$	$\sigma_y$	—	1	$i\sigma_x$
			$i\sigma_z$	
$\sigma_z$	$\sigma_z$	$i\sigma_y$	—	1
			$i\sigma_z$	

The matrices do not form a group since the products  $i\sigma_x$ ,  $i\sigma_y$ ,  $i\sigma_z$  and their negatives are not among the four given matrices.

12.9 All five  $d$  orbitals may contribute to bonding. (b) All except  $A_2(d_{xy})$  may participate in bonding.

12.11 (a)  $D_{2h}$ ; (b) (i) Staggered:  $\text{C}_{2h}$ ; (ii) Eclipsed:  $\text{C}_{2v}$ .

12.13 (a)  $\text{C}_{2v}$ ,  $f \rightarrow 2\text{A}_1 + \text{A}_2 + 2\text{B}_1 + 2\text{B}_2$ ;  
 (b)  $\text{C}_{3v}$ ,  $f \rightarrow \text{A}_1 + \text{A}_2 + 3\text{E}$ ;  
 (c)  $T_{\text{d}}$ ,  $f \rightarrow \text{A}_1 + \text{T}_1 + \text{T}_2$ ;  
 (d)  $\text{O}_{\text{h}}$ ,  $f \rightarrow \text{A}_{2\text{U}} + \text{T}_{1\text{U}} + \text{T}_{2\text{U}}$ .

Lanthanide ion (a) tetrahedral complex:  $f \rightarrow \text{A}_1 + \text{T}_1 + \text{T}_2$  in  $T_d$  symmetry, and there is one nondegenerate orbital and two sets of triply degenerate orbitals. (b) octahedral complex:  $f \rightarrow \text{A}_{2\text{U}} + \text{T}_{1\text{U}} + \text{T}_{2\text{U}}$ , and the pattern of splitting is the same.

12.15 irreducible representations:  $4\text{A}_1 + 2\text{B}_1 + 3\text{B}_2 + \text{A}_2$

## Chapter 13

T/K	$E/\text{J m}^{-3}$	$E_{\text{class}}/\text{J m}^{-3}$
(a) 1500	$2.136 \times 10^{-6}$	2.206
(b) 2500	$9.884 \times 10^{-4}$	3.676
(c) 5800	$3.151 \times 10^{-1}$	8.528

13.3  $\tau = \frac{1}{z} = \frac{kT}{4\sigma p} \left( \frac{\pi m}{kT} \right)^{1/2}$ ,  $\delta\nu \approx 700$  MHz, below 1 Torr.

13.5  $R_0 = 112.83$  pm,  $R_1 = 123.52$  pm.

13.7  $I = 2.728 \times 10^{-47}$  kg m<sup>2</sup>,  $R = 129.5$  pm, hence we expect lines at 10.56, 21.11, 31.67, ... cm<sup>-1</sup>.

13.9 218 pm.

13.11  $B = 14.35$  m<sup>-1</sup>,  $J_{\max} = 26$  at 298 K,  $J_{\max} = 15$  at 100 K.

13.13 linear.

13.15 (a) 5.15 eV; (b) 5.20 eV.

13.17 (a)  $\tilde{V} = 152$  m<sup>-1</sup>,  $k = 2.72 \times 10^{-4}$  kg s<sup>-2</sup>,  $I = 2.93 \times 10^{-46}$  kg m<sup>2</sup>,  $B = 95.5$  m<sup>-1</sup>.

(b)  $x_e = 0.96$ .

13.19 (a)  $C_{3v}$ ; (b) 9; (c)  $2A_1 + A_2 + 3E$ . (d) All but the  $A_2$  mode are infrared active. (e) All but the  $A_2$  mode may be Raman active.

13.23 (a) spherical rotor; (b) symmetric rotor; (c) linear rotor; (d) asymmetric rotor; (e) symmetric rotor; (f) asymmetric rotor.

13.25 HgCl<sub>2</sub>: 230, HgBr<sub>2</sub>: 240, HgI<sub>2</sub>: 250 pm.

13.27 (a) infrared active; (b) 796 cm<sup>-1</sup>; (c) O<sub>2</sub>: 2, O<sub>2</sub><sup>-</sup>: 1.5, O<sub>2</sub><sup>2-</sup>: 1; (d) Fe<sup>3+</sup>O<sub>2</sub><sup>2-</sup>; (e) Structures 6 and 7 are consistent with this observation, but structures 4 and 5 are not.

13.29  $s = 0.0768$  c,  $T = 8.34 \times 10^5$  K.

13.31  $B = 2.031$  cm<sup>-1</sup>;  $T = 2.35$  K.

## Chapter 14

14.1 49 364 cm<sup>-1</sup>.

14.3 14 874 cm<sup>-1</sup>.

14.5  $\mathcal{A} = 1.1 \times 10^6$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-2</sup>, Excitations from A<sub>1</sub> to A<sub>1</sub>, B<sub>1</sub>, and B<sub>2</sub> terms are allowed.

14.7 5.06 eV.

Hydrocarbon	$E_{\text{HOMO}}/\text{eV}^*$
Benzene	-9.7506
Biphenyl	-8.9169
Naphthalene	-8.8352
Phenanthrene	-8.7397
Pyrene	-8.2489
Anthracene	-8.2477

14.11 (a)  $\frac{n}{V} = 1.7 \times 10^{-9}$  mol dm<sup>-3</sup>, (b)  $N = 6.0 \times 10^2$ .

14.15 The transition moves toward the red as the chain lengthens and the apparent color of the dye shifts towards blue.

14.21 (a) 3 + 1, 3 + 3; (b) 4 + 4, 2 + 2.

14.23  $4.4 \times 10^3$ .

14.25  $\mathcal{A} = 1.24 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> dm<sup>-2</sup>.

14.27 (a)  $\mathcal{A} = 2.24 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-2</sup>; (b)  $A = 0.185$ ; (c)  $\epsilon = 135$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

14.29  $V_1 - V_0 = 3.1938$  eV,  $\tilde{V}_1 - \tilde{V}_0 = 79.538$  cm<sup>-1</sup>,  $\tilde{V}_0 = 2034.3$  cm<sup>-1</sup>,  $T_{\text{eff}} = 1321$  K.

## Chapter 15

15.1  $B_0 = 10.3$  T,  $\frac{\delta N}{N} \approx 2.42 \times 10^{-5}$ ,  $\beta$  state lies lower.

15.3  $300 \times 10^{-6}$  Hz  $\pm$  10 Hz, 0.29 s.

15.5 Both fit the data equally well.

15.9 Width of the CH<sub>3</sub> spectrum is  $3a_H = 6.9$  mT. The width of the CD<sub>3</sub> spectrum is  $6a_D$ . The overall width is  $6a_D = 2.1$  mT.

15.11  $P(\text{N}2s) = 0.10$ ,  $P(\text{N}2p_z) = 0.38$ , total probability:  $P(\text{N}) = 0.48$ ,  $P(\text{O}) = 0.52$ , hybridization ratio = 3.8,  $\Phi = 131^\circ$ .

15.13  $\sigma_d = \frac{e^2 \mu_0 Z}{12\pi m_e a_0} = 1.78 \times 10^{-5} Z$ .

15.15  $R = 158$  pm.

15.17  $I(\omega) \approx \frac{1}{2} \frac{A\tau}{1 + (\omega_0 - \omega)^2 \tau^2}$ .

15.21  $\frac{-g_I \mu_N \mu_0 m_I}{4\pi R^3} (\cos^2 \theta_{\max} + \cos \theta_{\max}), \langle \mathcal{B}_{\text{nucl}} \rangle = 0.58$  mT.

## Chapter 16

16.1  $W = 2 \times 10^{40}$ ,  $S = 1.282 \times 10^{-21}$  J K<sup>-1</sup>,  $S_1 = 0.637 \times 10^{-21}$  J K<sup>-1</sup>,  $S_2 = 0.645 \times 10^{-21}$  J K<sup>-1</sup>.

16.3  $\frac{\Delta W}{W} \approx 2.4 \times 10^{25}$ .

16.5  $T = 3.5 \times 10^{-15}$  K,  $q = 7.41$ .

16.7 (a) (i)  $q = 5.00$ ; (ii)  $q = 6.26$ ;

(b)  $p_0 = 1.00$  at 298 K,  $p_0 = 0.80$  at 5000 K;  $p_2 = 6.5 \times 10^{-11}$  at 298 K,  $p_2 = 0.12$  at 5000 K.

(c) (i)  $S_m = 13.38$  J K<sup>-1</sup> mol<sup>-1</sup>, (ii)  $S_m = 18.07$  J K<sup>-1</sup> mol<sup>-1</sup>.

16.9 (a)  $p_0 = 0.64$ ,  $p_1 = 0.36$ ; (b) 0.52 kJ mol<sup>-1</sup>. At 300 K,  $S_m = 11.2$  J K<sup>-1</sup> mol<sup>-1</sup>, At 500 K,  $S_m = 11.4$  J K<sup>-1</sup> mol<sup>-1</sup>.

16.11 (a) At 100 K:  $q = 1.049$ ,  $p_0 = 0.953$ ,  $p_1 = 0.044$ ,  $p_2 = 0.002$ ,  $U_m - U_m(0) = 123$  J mol<sup>-1</sup>,  $S_m = 1.63$  J K<sup>-1</sup> mol<sup>-1</sup>.

(b) At 298 K:  $q = 1.55$ ,  $p_0 = 0.645$ ,  $p_1 = 0.230$ ,  $p_2 = 0.083$ ,  $U_m - U_m(0) = 1348$  J mol<sup>-1</sup>,  $S_m = 8.17$  J K<sup>-1</sup> mol<sup>-1</sup>.

16.13 Most probable configurations are {2, 2, 0, 1, 0, 0} and {2, 1, 2, 0, 0, 0} jointly.

16.15 (a)  $T = 160$  K.

## Chapter 17

17.1 (a) 0.351; (b) 0.079; (c) 0.029.

17.3  $C_{V,m} = 4.2$  J K<sup>-1</sup> mol<sup>-1</sup>,  $S_m = 15$  J K<sup>-1</sup> mol<sup>-1</sup>.

17.5  $q = 19.90$ .

17.7  $S_m^{\ddagger} = 199.4$  J mol<sup>-1</sup> K<sup>-1</sup>.

17.11 At 298 K:  $K = 3.89$ . At 800 K:  $K = 2.41$ .

17.13 (a)  $\theta_R = 87.55$  K,  $\theta_V = 6330$  K.

17.16 (b)  $J_{\max} = \left( \frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2}$ ; (c)  $T \approx 374$  K.

17.17 (a)  $q^R = 660.6$ ; (b)  $q^R = 4.26 \times 10^4$ .

17.23  $S = 9.57 \times 10^{-15}$  J K<sup>-1</sup>.

17.25  $G_m^{\ddagger} - G_m^{\ddagger}(0) = 513.5$  kJ mol<sup>-1</sup>.

17.27 At 10 K,  $G_m^{\ddagger} - G_m^{\ddagger}(0) = 660.8$  J mol<sup>-1</sup>.

At 1000 K,  $G_m^{\ddagger} - G_m^{\ddagger}(0) = 241.5$  kJ mol<sup>-1</sup>.

## Chapter 18

18.1 (a)  $\epsilon = 1.1 \times 10^8$  V m<sup>-1</sup>; (b)  $\epsilon = 4 \times 10^9$  V m<sup>-1</sup>; (c)  $\epsilon = 4$  kV m<sup>-1</sup>.

18.3  $\alpha' = 1.2 \times 10^{-23}$  cm<sup>3</sup>,  $\mu = 0.86$  D.

18.5  $\alpha' = 2.24 \times 10^{-24}$  cm<sup>3</sup>,  $\mu = 1.58$  D,  $P'_m = 5.66$  cm<sup>3</sup> mol<sup>-1</sup>,  $\mu = 1.58$  D.

18.7 (a)  $\epsilon = 1.51 \times 10^{-23}$  J,  $R_e = 265$  pm.

**18.9**  $P_m = 8.14 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\epsilon_r = 1.76$ ,  $n_r = 1.33$ .

**18.19** (a)  $V = -39 \text{ J mol}^{-1}$ , (b) The force approaches zero as the distance becomes very large.

**18.21** (a)  $\mu = 1.03 \times 10^{-29} \text{ C m}$ ; (b)  $V_{\max} = 3.55 \times 10^{-23} \text{ J}$ .

## Chapter 19

**19.1**  $S = 4.97 \times 10^{-13} \text{ s}$  or  $5.0 \text{ Sv}$ .

**19.3**  $[\eta] = 0.0716 \text{ dm}^3 \text{ g}^{-1}$ .

**19.5**  $M = 158 \text{ kg mol}^{-1}$ .

**19.7** (a)  $K = 0.0117 \text{ cm}^3 \text{ g}^{-1}$  and  $a = 0.717$ .

**19.9**  $\bar{M}_n = 155 \text{ kg mol}^{-1}$ ,  $B = 13.7 \text{ m}^3 \text{ mol}^{-1}$ .

$$\text{19.13 } \bar{M}_n \approx \bar{M} + \left( \frac{2\gamma}{\pi} \right)^{1/2}.$$

**19.15** (a)  $R_{\text{rms}} = lN^{1/2}$ ,  $R_{\text{rms}} = 9.74 \text{ nm}$ ;

$$(b) R_{\text{mean}} = \left( \frac{8N}{3\pi} \right)^{1/2} l, R_{\text{mean}} = 8.97 \text{ nm};$$

$$(c) R^* = l \left( \frac{2}{3} N \right)^{1/2}, R^* = 7.95 \text{ nm};$$

$$\text{19.17 } (a) R_g = \left( \frac{3}{5} \right)^{1/2} a \quad (b) R_g = \frac{l}{2\sqrt{3}}. \text{ When } M = 100 \text{ kg mol}^{-1},$$

$R_g/\text{nm} = 2.40$ . For a rod of radius 0.50 nm,  $R_g = 46 \text{ nm}$ .

**19.23**  $v_p = 8v_{\text{mol}}$

For BSV,  $B = 28 \text{ m}^3 \text{ mol}^{-1}$ . For Hb,  $B = 0.33 \text{ m}^3 \text{ mol}^{-1}$ .

$$\text{For BSV, } \frac{\Pi - \Pi^*}{\Pi^*} = 2.6 \times 10^{-2} \text{ corresponding to 2.6 per cent.}$$

$$\text{For Hb, } \frac{\Pi - \Pi^*}{\Pi^*} = 5.0 \times 10^{-2} \text{ corresponding to 5 per cent.}$$

<b>19.25</b> (a) $\theta / {}^\circ$	20	45	90
$I_{\text{rod}} / I_{\text{cc}}$	0.976	0.876	0.514

(b)  $90^\circ$ .

**19.27**  $\bar{M}_n = 69 \text{ kg mol}^{-1}$ ,  $a = 3.4 \text{ nm}$ .

**19.29** pH = 3.85.

## Chapter 20

**20.1**  $\lambda = 118 \text{ pm}$ .

**20.3** Yes, the data support.

**20.5** face-centred cubic,  $a = 408.55 \text{ pm}$ ,  $\rho = 10.507 \text{ g cm}^{-3}$ .

**20.7**  $a(\text{KCl}) = 628 \text{ pm}$ , are broadly consistent.

**20.9**  $\rho = 7.654 \text{ g cm}^{-3}$ .

**20.11**  $\rho = 1.01 \text{ g cm}^{-3}$ .

**20.15**  $\rho = 1.385 \text{ g cm}^{-3}$ ,  $\rho_{\text{o.s.}} = 1.578 \text{ g cm}^{-3}$ .

**20.17** 0.736 eV.

**20.19** For  $S = 2$ ,  $\chi_m = 0.127 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ , For  $S = 3$ ,  $\chi_m = 0.254 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ , For  $S = 4$ ,  $\chi_m = 0.423 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ .

**20.21**  $x = 0.41$ .

**20.23** For a monoclinic cell,  $V = abc \sin \beta$ .

For an orthorhombic cell,  $V = abc$ .

**20.25**  $F_{hkl} \propto 1 + e^{5i\pi} + e^{6i\pi} + e^{7i\pi} = 1 - 1 + 1 - 1 = 0$ .

$$\text{20.31 } \xi = \frac{-e^2 a_0^2}{2m_e}, \chi_m = \frac{-N_A \mu_0 e^2 a_0^2}{2m_e}.$$

## Chapter 21

**21.3** (a)  $\langle h \rangle = 1.89 \text{ m}$ ; (b)  $\sqrt{\langle h^2 \rangle} = 1.89 \text{ m}$ .

**21.5**  $p = 7.3 \times 10^{-3} \text{ Pa}$ , or  $7.3 \text{ mPa}$ .

**21.7** (a) Cadmium:  $2 \times 10^{14} \text{ s}^{-1}$ ; (b) Mercury:  $1 \times 10^{17} \text{ s}^{-1}$ .

**21.9**  $\Lambda_m^o = 12.6 \text{ mS m}^2 \text{ mol}^{-1}$ ;  $\mathcal{K} = 7.30 \text{ mS m}^2 \text{ mol}^{-1} \text{ M}^{-1/2}$ .

(a)  $\Lambda_m = 11.96 \text{ mS m}^2 \text{ mol}^{-1}$ ; (b)  $\kappa = 119.6 \text{ mS m}^{-1}$ ; (c)  $R = 172.5 \Omega$ .

**21.11**  $s(\text{Li}^+) = 4.0 \times 10^{-3} \text{ cm s}^{-1}$ ,  $s(\text{Na}^+) = 5.2 \times 10^{-3} \text{ cm s}^{-1}$ ;  $s(\text{K}^+) = 7.6 \times 10^{-3} \text{ cm s}^{-1}$ .

$t(\text{Li}^+) = 250 \text{ s}$ ,  $t(\text{Na}^+) = 190 \text{ s}$ ,  $t(\text{K}^+) = 130 \text{ s}$ .

(a)  $d(\text{Li}^+) = 1.3 \times 10^{-6} \text{ cm}$ ;  $d(\text{Na}^+) = 1.7 \times 10^{-6} \text{ cm}$ ;  $d(\text{K}^+) = 2.4 \times 10^{-6} \text{ cm}$ .

(b) 43, 55 and 81 solvent molecule diameters respectively.

**21.13**  $t_+ = 0.48$  and  $t_- = 0.52$ .  $u_+ = 7.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ .  $\lambda_+ = 72 \text{ S cm}^2 \text{ mol}^{-1}$ .

**21.15** (a)  $2.1 \times 10^{-20} \text{ N molecule}^{-1}$ ; (b)  $2.8 \times 10^{-20} \text{ N molecule}^{-1}$ ; (c)  $4.1 \times 10^{-20} \text{ N molecule}^{-1}$ .

**21.17** 9.3 kJ mol<sup>-1</sup>.

**21.19**  $1.2 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ .

**21.21** (a)  $3.68 \times 10^{-10} \text{ m}$ ; (b)  $3.07 \times 10^{-10} \text{ m}$ .

**21.25**  $\langle v_x \rangle = 0.47 \langle v_x \rangle_{\text{initial}}$ .

$$\text{21.27 } \frac{f(nc^*)}{f(c^*)} = \frac{(nc^*)^2 e^{-mn^2 c^* / 2kT}}{c^{*2} e^{-mc^{*2} / 2kT}} [24.4] = n^2 e^{-(n^2 - 1)mc^{*2} / 2kT} = n^2 e^{(1-n^2)}$$

$$\frac{f(3c^*)}{f(c^*)} = 3.02 \times 10^{-3}, \frac{f(4c^*)}{f(c^*)} = 4.9 \times 10^{-6}.$$

**21.31** (a)  $p = 0$ ; (b)  $p = 0.016$ ; (c)  $p = 0.054$ .

**21.37** The total energy density (translational plus rotational) =  $\rho T = 0.25 \text{ J cm}^{-3}$ .

**21.39**  $t = 10^8 \text{ s}$ .

## Chapter 22

**22.1** Second-order,  $k = 0.0594 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ ,  $m = 2.94 \text{ g}$ .

**22.3** First-order,  $k = 1.23 \times 10^{-4} \text{ s}^{-1}$ .

**22.5**  $9.70 \times 10^4 \text{ J mol}^{-1}$ .

**22.7**  $k = 3.65 \times 10^{-3} \text{ min}^{-1}$ ,  $t_{1/2} = 190 \text{ min}$ .

**22.9**  $k = 2.37 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $t_{1/2} = 4.98 \times 10^{-3} \text{ s}$ .

**22.11** Propene: first order, HCl: third-order.

**22.13** rate =  $k K_1 K_2 [\text{HCl}]^3 [\text{CH}_3\text{CH}=\text{CH}_2]$ ; look for evidence of proposed intermediates, e.g. using infrared spectroscopy to search for  $(\text{HCl})_2$ .

**22.15**  $E_{\text{a,eff}} = -18 \text{ kJ mol}^{-1}$ ,  $E_{\text{a}} = +10 \text{ kJ mol}^{-1}$ .

**22.17** There are marked deviations at low pressures, indicating that the Lindemann theory is deficient in that region.

**22.19** The product concentration ratio increases.

$$\text{22.23 } (a) kt = \frac{2x(A_0 - x)}{A_0^2(A_0 - 2x)^2}; (b) kt = \left( \frac{2x}{A_0^2(A_0 - 2x)} \right) + \left( \frac{1}{A_0^2} \right) \ln \left( \frac{A_0 - 2x}{A_0 - x} \right)$$

$$\text{22.27 } v_{\text{max}} = k \left( \frac{[A]_0 + [B]_0}{2} \right)^2;$$

**22.29** 2720 y.

**22.31** (a) First-order, (b)  $k = 0.00765 \text{ min}^{-1} = 0.459 \text{ h}^{-1}$ ,  $t_{1/2} = 1.5 \text{ h} = 91 \text{ min}$ .

$$\text{22.35 } v = k[A][B], k = \frac{k_1 k_2}{k'_1}.$$

**22.37**  $E_{\text{a}} = 13.9 \text{ kJ mol}^{-1}$ ,  $A = 1.03 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

$$\text{22.39 } k_1 = 3.82 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
,  $k_2 = 5.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_3 = 4.17 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $\frac{k_2}{k_1} = 0.13$ .

## Chapter 23

**23.3** (1) Initiation, (2), (3), (4) and (5) Propagation, (6) Termination.

$$\frac{d[SiH_4]}{dt} = \left( \frac{k_1 k_4 k_5}{k_6} \right)^{1/2} [N_2O][SiH_4]^{1/2}$$

**23.5**  $\frac{d[HI]}{dt} = \frac{2k_b k_a [I_2][H_2]}{k'_a + k_b[H_2]}$ . This simple rate law is observed when step (b) is rate-determining so that step (a) is a rapid equilibrium and  $[I]$  is in an approximate steady state. This is equivalent to  $k_b[H_2] = k'_a$  and hence,  $\frac{d[HI]}{dt} = 2k_b K[I_2][H_2]$ .

**23.7** (a)  $\tau_0 = 6.67$  ns; (b)  $k_f = 0.105$  ns $^{-1}$ .

**23.9**  $k_q = 1.98 \times 10^9$  dm $^3$  mol $^{-1}$  s $^{-1}$ .

**23.13**  $\delta M = \frac{p^{1/2} M}{1 - p}$ ,  $\delta M = M \{kt[A]_0(1 + kt[A]_0)\}^{1/2}$ .

**23.15**  $\langle n \rangle = v = k[M][I]^{1/2}$ .

**23.19**  $\frac{d[A]}{dt} = -I - k_2 \left( \frac{I}{k_3} \right)^{1/2} [A]$ .

**23.21**  $f = \frac{k_2 k_4 [CO]}{k_2 [CO] + k_3 [M]}$ .

**23.27** Uncompetitive.

**23.29**  $R = 2.6$  nm.

**23.35** (a) Initiation, propagation, propagation, termination, initiation;

$$(b) \frac{d[NO]}{dt} = -2k_a[NO]^2 - 2k_b[O][NO];$$

$$(c) E_{a,eff} = E_b + \frac{1}{2}E_{-d} - \frac{1}{2}E_d;$$

$$(d) E_{a,eff} \approx 381.39 \text{ kJ mol}^{-1};$$

$$(e) \frac{d[NO]}{dt} = -2k_b \left( \frac{k_a}{2k_d[M]} \right)^{1/2} [NO]^2;$$

$$(f) \frac{d[NO]}{dt} = -2k_b \left( \frac{k_a}{2k_d[M]} \right)^{1/2} [NO]^2, \text{ where } k_s \text{ is the rat constant}$$

for  $NO + O_2 \rightarrow O + NO_2$ ,  $E_{a,eff} = 253$  kJ mol $^{-1}$ , this value is consistent with the low range of the experimental values of  $E_{a,eff}$ .

## Chapter 24

**24.1** (a)  $\sigma^* = 4.4 \times 10^{-20}$  m $^2$ ; (b)  $P = 0.15$ .

**24.3**  $k_2 = 1.7 \times 10^{11}$  M $^{-1}$  s $^{-1}$ ,  $t = 3.6$  ns.

**24.5** 2–.

**24.9** (a)  $-\frac{d[F_2O]}{dt} = k_1[F_2O]^2 + k_2 \left( \frac{k_1}{k_4} \right)^{1/2} [F_2O]^{3/2}$ ; (b)  $\Delta H(FO-F) \approx$

$$E_1 = 160.9 \text{ kJ mol}^{-1}, \Delta H(O-F) \approx 224.4 \text{ kJ mol}^{-1}, E_2 \approx 60 \text{ kJ mol}^{-1}$$

**24.11** Linear regression analysis of  $\ln(\text{rate constant})$  against  $1/T$  yields the following results:  $R = 0.999\ 76$  and  $R = 0.998\ 48$ , which indicate that the data are a good fit.

**24.15**  $P = 5.2 \times 10^{-6}$ .

**24.17**  $k_1 = \frac{v^3}{v^{\frac{3}{2}}} e^{-\beta \Delta E_0}$ , (a)  $D = 2.7 \times 10^{-15}$  m $^2$  s $^{-1}$ , (b)  $D = 1.1 \times 10^{-14}$  m $^2$  s $^{-1}$ .

**24.23** For O<sub>2</sub> with ethyl:  $P = 1.6 \times 10^{-3}$ ; For O<sub>2</sub> with cyclohexyl:  $P = 1.8 \times 10^{-3}$ .

**24.25**  $z_A = +3.0$ .

**24.27** Yes, the equation appears to apply,  $\beta = 13.4$  nm $^{-1}$ .

## Chapter 25

**25.1** For a cation above a flat surface, the energy is 0.11. For a cation at the foot of a high cliff, the energy is –0.51. The latter is the more likely settling point.

**25.3** (a)  $1.61 \times 10^{15}$  cm $^{-2}$ ; (b)  $1.14 \times 10^{15}$  cm $^{-2}$ ; (c)  $1.86 \times 10^{15}$  cm $^{-2}$ .

For the collision frequencies:

$Z/(atom^{-1} s^{-1})$	Hydrogen		Propane	
	100 Pa	$10^{-7}$ Torr	100 Pa	$10^{-7}$ Torr
(100)	$6.8 \times 10^5$	$8.7 \times 10^{-2}$	$1.4 \times 10^5$	$1.9 \times 10^{-2}$
(110)	$9.6 \times 10^5$	$1.2 \times 10^{-1}$	$2.0 \times 10^5$	$2.7 \times 10^{-2}$
(111)	$5.9 \times 10^5$	$7.5 \times 10^{-2}$	$1.2 \times 10^5$	$1.7 \times 10^{-2}$

**25.5** (a)  $c = 164$ ,  $V_{mon} = 13.1$  cm $^3$ ; (b)  $c = 264$ ,  $V_{mon} = 12.5$  cm $^3$ .

**25.7**  $c_2 = 2.4$ ,  $c_1 = 0.16$ .

**25.9**  $K = 0.138$  mg g $^{-1}$ ,  $n = 0.58$ .

**25.11**  $n_\infty = 5.78$  mol kg $^{-1}$ ,  $K = 7.02$  Pa $^{-1}$ .

**25.13**  $j_0/(mA \text{ cm}^{-2}) = 0.78$ ,  $\alpha = 0.38$ .

**25.15**  $\delta = 2.5 \times 10^{-4}$  m or 0.25 mm.

**25.21** (a) The Tafel plot of  $\ln j$  against  $E$  show no region of linearity so the Tafel equation cannot be used to determine  $j_0$  and  $\alpha$ .

**25.31** BET isotherm is a much better representation of the data.  $V_{mon} = 75.4$  cm $^3$ ,  $c = 3.98$ .

**25.33** (a) R values in the range 0.975 to 0.991, the fit is good at all temperatures.

(b)  $k_a = 3.68 \times 10^{-3}$ ,  $\Delta_{ad}H = -8.67$  kJ mol $^{-1}$ ,  $k_b = 2.62 \times 10^{-5}$  ppm $^{-1}$ ,  $\Delta_qH = -15.7$  kJ mol $^{-1}$ .

(c)  $k_a$  may be interpreted to be the maximum adsorption capacity at an adsorption enthalpy of zero, while  $k_b$  is the maximum affinity in the case for which the adsorbant–surface bonding enthalpy is zero.

**25.35** (a)  $K$  unit:  $(g_R \text{ dm}^{-3})^{-1}$  [ $g_R$  = mass (grams) of rubber],  $K_F$  unit:  $(mg)^{(1-1/n)} g_R^{-1} \text{ dm}^{-3/n}$ ,  $K_L$  unit:  $(mg \text{ dm}^{-3})^{-1}$ ,  $M$  unit:  $(mg \text{ g}_R^{-1})$ .

(b)  $R$  (Linear) = 0.9612,  $R$  (Freudlich) = 0.9682,  $R$  (Langmuir) = 0.9690, on this basis alone, the fits are equally satisfactory, but not good. The Langmuir isotherm can be eliminated as it gives a negative value for  $K_L$ : the fit to the Freudlich isotherm has a large standard deviation. Hence the linear isotherm seems the best fit, but the Freudlich isotherm is preferred for this kind of system.

(c)  $q_{rubber}/q_{charcoal} = 0.164 c_{eq}^{-0.46}$ , hence much worse.

**25.37** (a) Therefore, the metals with a thermodynamic tendency to corrode in moist conditions at pH = 7 are Fe, Al, Co, Cr if oxygen is absent, but, if oxygen is present, all seven elements have a tendency to corrode.

(b) Ni: corrodes, Cd: corrodes, Mg: corrodes, Ti: corrodes, Mn: corrodes.

**25.39** 0.28 mg cm $^{-2}$ d $^{-1}$ .

# Index

(T) denotes a table in the Data Section.

## A

$A_2$  spectrum 531  
*ab initio* method 394  
absolute value 963  
absorbance 432  
absorption spectroscopy 431  
abundant-spin species 541  
acceleration 981  
acceleration of free fall 979  
acceptable wavefunction 272  
accommodation 917  
acetaldehyde pyrolysis 830  
achiral molecule 412  
acid 763  
acid catalysis 839  
acidity constant 763, (T) 1007  
acronyms 950  
activated complex 809, 881  
activated complex theory 880  
activation, enthalpy of 51  
activation energy 807, (T) 1023  
  composite reaction 822  
  negative 822  
activation Gibbs energy (electrode) 935  
activation-controlled reaction 877  
active site 840  
active transport 770  
activity 158, 204  
  ion 163  
activity coefficient 159  
  determination 228  
additional work 34, 99  
adiabat 48  
adiabatic bomb calorimeter 38  
adiabatic boundary 6  
adiabatic demagnetization 568  
adiabatic expansion 47, 48, 69  
adiabatic flame calorimeter 42  
adiabatic nuclear demagnetization 568  
adiabatic process, entropy change 80  
ADP 224, 225  
adsorbate 909  
adsorbent 909  
adsorption 909  
adsorption isotherm 917  
adsorption rate 923  
aerobic metabolism 225  
aerosol 682  
AES 914  
AFM 289, 637  
air, composition 11

Airy radius 466  
all-*trans*-retinal 490  
allowed transition 335, 435  
alloy 175  
  microstructure 191  
alpha-helix 677  
alveoli 147  
amount of substance 959  
amplitude 982  
anaerobic metabolism 225  
angstrom 961  
angular momentum 297, 981  
  commutator 307  
  magnitude 305  
  operator 307  
  orbital 326  
  quantization 298  
  summary of properties 309  
  total 349, 352  
z-component 306  
angular velocity 981  
anharmonic 455  
anharmonicity constant 455  
anode 217  
anodic current density 935  
anti-parallel beta-sheet 678  
anti-Stokes radiation 431  
anti-bonding orbital 371  
anticyclone 12  
antiferromagnetic phase 736  
antioxidant 386  
antisymmetric stretch 461  
antisymmetric wavefunction 338  
apomyoglobin 819  
aragonite 43  
area 966  
argon viscosity 760  
argon-ion laser 507  
aromatic stability 392  
array detector 470  
Arrhenius equation 807  
Arrhenius parameters 807, 873, (T) 1021  
ascorbic acid 386  
asymmetric rotor 442  
asymmetry potential 230  
asymptotic solution 323  
atmosphere 11, 462  
  temperature 463  
  temperature profile 854  
atmosphere (unit) 4, 961  
atmosphere composition 853  
atmospheric ozone 855  
atom 320  
  configuration 337  
  many-electron 336  
  selection rule 335  
  term symbol 352

atomic force microscopy 289, 637  
atomic level 349  
atomic orbital 326  
atomic weight 959  
atomization, enthalpy of 51  
ATP 224, 858  
attractive surface 890  
*Aufbau* principle, see building-up principle 340  
Auger electron spectroscopy 914  
autocatalysis 803  
autoprotolysis rate 806  
avalanche photodiode 473  
average molar mass 653  
average value 528, 966  
Avogadro's principle 7  
AX energy levels 524  
 $AX_2$  spectrum 526  
 $AX_3$  spectrum 526  
Axilrod-Teller formula 636  
axis of improper rotation 406  
axis of symmetry 405  
azeotrope 184  
azimuth 301

## B

Balmer series 320  
band formation 724  
band gap 725  
band head 487  
band spectra 457  
band width 725  
bar 4, 961  
barometer 4  
barometric formula 12  
barrier penetration 286  
barrier transmission 287  
base 763  
base catalysis 840  
base pairs 680  
base-stacking 681  
base unit 960  
basis set 380  
Bayard-Alpert pressure gauge 5  
Beer-Lambert law 432  
bends, the 147  
benzene, MO description 391  
Berthelot equation of state 19  
BET isotherm 920  
beta-barrel 679  
beta-pleated sheet 678  
beta-sheet 678  
bilayer 686  
bimolecular reaction 810  
binomial coefficient 973  
binomial expansion 571, 973  
biochemical cascade 491  
biofuel cell 948  
biological standard state 161, 209  
biosensor analysis 925  
bipolaron 674  
Birge-Sponer plot 456  
bivariate 176  
black body 245  
black-body radiation 245  
block-diagonal matrix 414  
Blodgett, K. 687  
blue sky 658  
body-centred unit cell 699  
Bohr frequency condition 249  
Bohr magneton 514  
Bohr model 360  
Bohr radius 324  
boiling 118  
boiling point (T) 990  
boiling point constant 151, (T) 1004  
boiling temperature 118  
Boltzmann distribution 81, 208, 563, 582  
  chemical equilibrium 212  
Boltzmann formula 81, 575, 583  
Boltzmann, L. 81  
bond 362  
bond dissociation energy 377  
bond dissociation enthalpy 377, (T) 1011  
bond enthalpy 55  
bond length (T) 1011  
  determination 448  
bond order 376  
bond order correlations 377  
bond torsion 676  
bonding orbital 370  
Born equation 102, 110  
Born interpretation 256, 272  
Born, M. 102, 256  
Born-Mayer equation 719  
Born-Haber cycle 719  
Born-Oppenheimer approximation 363, 473  
boson 309, 338  
bouncing ball 77  
bound state, hydrogen atom 326  
boundary 5  
boundary condition 278, 971  
  cyclic 298  
boundary surface 329, 369  
Boyle temperature 16  
Boyle's law 7  
bra 313  
bracket notation 313  
Brackett series 321  
Bragg, W. and L. 704  
Bragg's law 704  
branch 458, 487

branching step 833  
 brass 131  
 Bravais lattice 699  
 breathing 147  
*Bremsstrahlung* 702  
 Brønsted acid 763  
 Brønsted base 763  
 Brunauer, S. 920  
 bubble 642  
 buckminsterfullerene 410  
 building-up principle 340  
 bulk modulus 722  
 bumping 645  
 butadiene, MO description 389

---

**C**

caesium-chloride structure 717  
 cage effect 876  
 calamitic liquid crystal 189  
 calcite 43  
 calorie 31, 979  
 calorimeter 38  
 calorimeter constant 38  
 calorimetry 38  
 camphor 628  
 candela 960  
 canonical distribution 578  
 canonical ensemble 577  
 canonical partition function 578  
 capacitance manometer 5  
 capillary action 643  
 capillary electrophoresis 664  
 capillary technique 778  
 carbon dioxide  
     isotherm 15  
     phase diagram 120  
     supercritical 119  
     vibrations 461  
 carbon dioxide laser 507  
 carbon monoxide, residual entropy 610  
 carbon nanotube 728  
 carbonyl group 489  
 Carnot cycle 82  
 carotene 281, 398, 857  
 CARS 465  
 casein 682  
 catalyst 839  
 catalyst properties 930  
 catalytic constant 842  
 catalytic efficiency 842  
 catalytic hydrogenation 930  
 catalytic oxidation 930  
 cathode 217  
 cathodic current density 935  
 cathodic protection 950  
 cavity 642  
 CCD 473  
 CCP 716  
 CD spectra 491  
 cell, electrochemical 216  
 cell emf 219

cell notation 218  
 cell overpotential 944  
 cell potential 219  
 cell reaction 218  
 Celsius scale 6  
 centre of symmetry 406  
 centrifugal distortion 446  
 centrifugal distortion constant 446  
 centrifugal effect 323  
 ceramic 736  
 caesium, see caesium 717  
 CFC 855  
 chain carrier 830  
 chain polymerization 835, 836  
 chain reaction 830  
 chain relation 68, 968  
 chain rule 966  
 chain transfer 837  
 chain-branching explosion 833  
 channel former 770  
 Chapman model 855  
 character 413  
 character table 413, (T) 1023  
 characteristic rotational temperature 594  
 characteristic vibrational temperature 597  
 charge-coupled device 473  
 charge transfer rate 934  
 charge-transfer transition 489  
 Charles's law 7  
 chemical equilibrium 208  
     Boltzmann distribution 208, 212  
 chemical exchange 532, 533  
 chemical kinetics 791  
 chemical potential 122  
     chemical equilibrium 201  
     general definition 138  
     significance 139  
     standard 141  
     variation with pressure 123  
     variation with temperature 123  
 chemical potential (band theory) 726  
 chemical potential gradient 772  
 chemical quench flow method 794  
 chemical shift 519  
     electronegativity 522  
     typical 520  
 chemiluminescence 886  
 chemiosmotic theory 227  
 chemisorption 917  
 chemisorption ability 929  
 chiral molecule 412, 491  
 chlorofluorocarbon 855  
 chlorophyll 856, 857  
 chloroplast 254, 856  
 cholesteric phase 189  
 cholesterol 687  
 chorine atom ozone decomposition 855  
 CHP system 947  
 chromatic aberration 490  
 chromatography 119  
 chromophore 487, (T) 1014  
 chromosphere 346  
 chronopotentiometry 940  
 circular dichroism 491  
 circular polarization 491  
 circularly birefringent 985  
 circularly polarized 984  
 circumstellar space 480  
*cis*-retinal 490, 853  
 citric acid cycle 225, 856  
 Clapeyron equation 126  
 class 415, 416  
 classical mechanics 243  
 clathrate 635  
 Clausius inequality 86, 95  
 Clausius–Clapeyron equation 128  
 Clausius–Mossotti equation 627  
 Clebsch–Gordan series 352  
 close-packed 715  
 closed shell 339  
 closed system 28  
 cloud colour 658  
 cloud formation 645  
 CMC 685  
 CNDO 394  
 co-adsorption 926  
 coagulation 684  
 COBE 438  
 coefficient of performance 85  
 coefficient of thermal conductivity 758  
 coefficient of viscosity 758, 759, 785  
 cofactor (matrix) 976  
 coherence length 497  
 coherent anti-Stokes Raman spectroscopy 465  
 coherent radiation 497  
 colatitude 301  
 cold denaturation 819  
 collapse pressure 688  
 colligative property 150  
 collision 9, 753  
     elastic 748  
     reactive 886  
 collision cross-section 753, 870, (T) 1018  
 collision density 870  
 collision diameter 753  
 collision flux 755  
 collision frequency 753, 755  
 collision theory 809, 870  
 collision-induced emission 846  
 collisional deactivation 438, 846  
 collisional lifetime 438  
 colloid 682  
 colloid stability 683  
 colour 481, (T) 1013  
 column vector 976  
 combination difference 458  
 combination principle 321  
 combinatorial function 973  
 combined gas law 10  
 combined heat and power system 947  
 combustion, enthalpy of 51  
 common logarithm 963  
 commutator 271  
     angular momentum 307  
 commute 271  
 competitive inhibition 844  
 complementary observable 271  
 complete neglect of differential overlap 394  
 complete set 267  
 complete shell 339  
 complex conjugate 256, 963  
 complex mode process 891  
 complex number 256, 963  
 component 175  
 compound semiconductor 726  
 compressibility 722  
 compression factor 14, 111  
 Compton wavelength 316  
 computational chemistry 393  
 concentration cell 218  
 concentration polarization 941  
 concentration profile 878  
 condensation 17, 645  
 conductance 761  
 conducting polymer 674  
 conductivity 762  
     thermal 758  
 configuration  
     atom 337  
     macromolecule 667  
     statistical 561  
 configuration integral 604  
 confocal microscopy 504  
 conformation 667  
 conformational conversion 532  
 conformational energy 675  
 conformational entropy 671  
 congruent melting 192  
 conjugated polyene 401  
 consecutive reactions 811  
 consolute temperature 186  
 constant  
     acidity 763  
     anharmonicity 455  
     boiling point 151  
     calorimeter 38  
     centrifugal distortion 446  
     critical 16  
     dielectric 110  
     equilibrium 203  
     Faraday's 985  
     force 452, 982  
     freezing point 153  
     gas 8  
     Lamé 743  
     Madelung 719  
     Michaelis 841  
     normalization 255  
     Planck's 246  
     rotational 443

Rydberg 320, 327  
 scalar coupling 524  
 second radiation 275  
 spin-orbit coupling 350  
 time 801  
 constituent 175  
 constrained chain 672  
 constructive interference 370  
 contact angle 644  
 continuum generation 503  
 contour diagram (reaction) 887  
 contour length 670  
 convection 12, 777  
 convective flux 777  
 cooling 86  
 cooling curve 178, 191  
 Cooper pair 737  
 cooperative transition 572  
 coordination 717  
 coordination number 716  
 core hamiltonian 393  
 Corey-Pauling rules 675  
 corona 346  
 correlation analysis 884  
 correlation diagram 355  
 correlation spectroscopy 543  
 corresponding states 21  
 corrosion 948  
 corrosion current 949  
 Cosmic Background Explorer 438  
 cosmic ray 244, 984  
 COSY 543  
 Coulomb integral 380  
 Coulomb interaction 986  
 Coulomb operator 393  
 Coulomb potential 110, 986  
   shielded 167  
 Coulomb potential energy 986  
 counter electrode 939  
 covalent bond 362  
 covalent network solid 720  
 cracking 931  
 cream 682  
 critical compression factor 21  
 critical constant 16, 17  
 critical field 737  
 critical isotherm 15  
 critical micelle concentration 685  
 critical molar volume 17  
 critical point 17  
 critical pressure 17, 118  
 critical solution temperature 186  
 critical temperature 17, 118  
 cross-peaks 546  
 cross-product 965  
 cross-relation 900, 903  
 cross-section 753, 870  
   state-to-state 887  
 crossed-beam technique 648  
 crossed molecular beams 886  
 cryogenics 568  
 crystal diode 473  
 crystal structure 697, 715

crystal system 698  
 crystallinity 673  
 crystallographic point group 408  
 crystallography 711  
 cubic close packed 716  
 cubic F 716  
 cubic group 410  
 cubic unit cell 698  
 cumulative reaction probability 891  
 Curie law 734  
 Curie temperature 736  
 current 987  
 current density 909  
 curvature 264  
 curved surface 643  
 CW spectrometer 520  
 cyclic boundary condition 301  
 cyclic voltammetry 943  
 cyclone 12  
 cytochrome 228  
 cytosol 771

**D**

*d* block 342  
*D* lines 351  
*d* orbital 334  
*d* orbital hybridization 367  
*d-d* transition 484, 487  
*d*-metal complex 488  
 Dalton's law 13, 179  
 Daniell cell 218  
 dark current 473  
 Davisson, C. 252  
 Davisson-Germer experiment 252  
 Davydov splitting 730  
 de Broglie relation 252, 278  
 de Broglie wavelength 570  
 de Broglie, L. 252  
 Debye equation 627  
 Debye extrapolation 91  
 Debye formula 248  
 Debye length 168  
 Debye  $T^3$  law 91  
 Debye temperature 248  
 Debye, P. 248, 703  
 Debye-Hückel limiting law 164  
 Debye-Hückel theory 164, 167, 222  
 Debye-Hückel-Onsager coefficient  
   (T) 1019  
 Debye-Hückel-Onsager theory 769  
 decomposition vapour pressure 206  
 defect surface 910  
 definite integral 966  
 degeneracy 416  
   rotational 445  
 degenerate 286  
 degenerate orbital 334  
 degradation 668  
 degree of conversion 572  
 degree of deprotonation 763  
 degree of dissociation 207, 211  
 degree of freedom 176

degree of ionization 763  
 degree of polymerization 835  
 delocalization energy 390  
 delta scale 519  
 denaturation 198, 668, 681, 819  
 density (T) 990  
 density functional theory 397  
 density of states 245, 744  
 depolarization 464  
 depression of freezing point 151  
 derivative 966  
 derived unit 960  
 derived units 961  
 Derjaguin, B. 683  
 deshielded nucleus 519  
 desorption 909  
 desorption rate 923  
 destructive interference 372  
 detection period 543  
 detector 471, 473  
 determinant 382, 975  
 deuterium lamp 470  
 DFT 395  
 diagonal peaks 546  
 dialysis 155, 712  
 diamagnetic 377, 734  
 diamagnetic contribution 521  
 diamond structure 720  
 diamond-anvil cell 178  
 diathermic boundary 5  
 diatomic molecule (T) 1013  
 diatomic molecule spectra 482  
 dielectric 619  
 dielectric constant 110, (T) 1004  
 Dieterici equation of state 19  
 differential 968  
 differential equation 811, 971  
 differential overlap 394  
 differential pulse voltammetry 943  
 differential scanning calorimeter 46  
 differential scattering cross-section  
   640  
 differentiation 966  
 diffraction 702  
 diffraction grating 471  
 diffraction limit 466  
 diffraction order 471  
 diffraction pattern 702  
 diffractometer 703  
 diffuse double layer 933  
 diffusion 747, 757, 772, 776  
   reaction 877, 879  
   relation to curvature 777  
   relation to mobility 774  
 diffusion coefficient 758, 759, 784,  
   (T) 1016  
   viscosity 775  
 diffusion equation 877  
 diffusion-controlled limit 877  
 dihelium 373  
 dilute-spin species 541  
 diode laser 732  
 dioxygen, electronic states 483

dipole 620  
 dipole moment 620, (T) 1015  
   induced 624  
   measurement 446  
 dipole-charge interaction 629  
 dipole-dipole interaction 631, 646  
 dipole-dipole interaction (EPR) 553  
 dipole-induced dipole interaction  
   633

Dirac bracket notation 313  
 direct method 710  
 direct mode process 891  
 direct product decomposition 420  
 discotic liquid crystal 189  
 dismutation 385  
 disorder 81  
 disperse phase 682  
 dispersing element 432, 471  
 dispersion 81, 175, 985  
 dispersion interaction 633, 677  
 disproportionation 837  
 dissociation 495  
   degree of 207, 211  
 dissociation energy 363  
   determination 456  
 dissociation equilibrium 612  
 dissociation limit 495  
 distillation 182  
   partially miscible liquids 187  
 distinguishable molecules 580  
 distortion polarization 626  
 distribution of speeds 749  
 disulfide bond 681  
 DNA 652, 680  
   analysis 664  
   damage 855  
   intercalation 638  
   structure from X-rays 711  
 Dogonadze, R.R. 896  
 donor-acceptor pair 852  
 dopant 726  
 doping 191  
 Doppler broadening 436  
 Doppler effect 361, 436  
 dot product 350, 514, 965  
 drift speed 661, 765, 774  
 droplet 642  
 drug design 638  
 dry air 11  
 DSC 42  
 duality 253  
 Dulong and Petit law 247  
 Dulong, P.-L. 247  
 dust grain 438  
 DVLO theory 684  
 dye laser 508  
 dynamic light scattering 660  
 dynode 473

**E**

Eadie-Hofstee plot 867  
 Earth surface temperature 463

- eddy 11  
 edible fat 930  
 EELS 913  
 effect 769  
     cage 876  
     centrifugal 323  
     Doppler 361, 436  
     electrophoretic 769  
     Joule–Thomson 64  
     kinetic isotope 816  
     kinetic salt 885  
     Meissner 737  
     photoelectric 250  
     relaxation 769  
     salting-in 173  
     salting-out 173  
     Stark 446  
 effective mass 453  
 effective nuclear charge 339, (T)  
     1009  
 effective potential energy 323  
 effective transverse relaxation time  
     538  
 efficiency 83, 585  
 effusion 747  
 Ehrenfest classification 129  
 Ehrenfest equations 134  
 eigenfunction 262  
 eigenvalue 262  
 eigenvalue equation 261, 977  
 eigenvector 977  
 Einstein, A. 247  
 Einstein coefficient 434  
 Einstein formula 602  
 Einstein formula (heat capacity) 247  
 Einstein relation 774  
 Einstein temperature 247  
 Einstein–Smoluchowski equation 782  
 elastic collision 9  
 elastic deformation 720  
 elastic limit 723  
 elastomer 673  
 electric conduction 747  
 electric dipole 620  
 electric field 244, 631, 983  
 electric field strength 987  
 electric potential 110  
 electrical conductivity, temperature  
     dependence 726  
 electrical double layer 683, 932  
 electrical heating 38  
 electrical power 38, 987  
 electro-osmotic drag 948  
 electroactive species 909  
 electrochemical cell 216  
 electrochemical correlations 397  
 electrochemical potential 952  
 electrochemical series 224  
 electrode 216  
     counter 939  
     reference 939  
     varieties 216  
     working 939  
 electrode compartment 216  
 electrode concentration cell 218  
 electrode potential 941, 952  
 electrode process 932  
     electrode, varieties of 216  
     electrode–surface interface 932  
     electrodialysis 683  
     electrokinetic potential 683  
     electrolysis 944  
     electrolyte 216, 762  
     electrolyte concentration cell 218  
     electrolytic cell 216  
     electromagnetic field 243, 983  
     electromagnetic radiation 491  
     electromagnetic spectrum 244, 984  
     electromotive force 219  
     electron, magnetic moment 514  
     electron affinity 344  
         periodicity 344  
     electron affinity (T) 1010  
     electron density 396, 708  
     electron diffraction 252, 714  
     electron energy loss spectroscopy  
         913  
     electron gain  
         electrical 51  
         enthalpy of 51  
     electron in magnetic field 514  
     electron interaction integrals 371  
     electron microscopy 253  
     electron pair 337  
     electron pair formation 364  
     electron paramagnetic resonance  
         516, 549  
     electron scattering factor 742  
     electron spectroscopy for chemical  
         analysis 913  
     electron spin resonance 516, 549  
     electron transfer  
         between proteins 900  
         reaction 853, 894  
     electron-gain enthalpy 343  
     electronegativity 379, (T) 1012  
     electronic partition function 597  
     electronic polarizability 626  
     electronic structure 320  
     electronvolt 961  
     electrophoresis 663  
     electrophoretic effect 769  
     electrostatic potential surface 396  
     electrostatics 985  
     elementary reaction 809  
     elevation of boiling point 150  
     Eley–Rideal mechanism 928  
     Ellingham diagram 215  
     elpot surface 396  
     emf 219  
         temperature variation 231  
     emission spectroscopy 431  
     Emmett, P. 920  
     emulsification 683  
     emulsion 682  
     end separation (polymer) 669  
     energonic 202  
     endothermic process 29  
     energy 29, 979  
         conformational 675  
         electron in magnetic field 514  
         harmonic oscillator 291  
         multipole interaction 630  
         nucleus in magnetic field 515  
         particle in a box 280  
         quantization 246, 260  
         rotational 443  
         zero-point 281  
     energy density 755  
     energy dispersal 77  
     energy flux 757  
     energy pooling 846  
     ensemble 577  
     enthalpy 40  
         electron gain 343  
         ionization 343  
         partition function 590  
         reaction 212  
         variation with temperature 46  
     enthalpy and entropy, relation  
         between 44  
     enthalpy density 53  
     enthalpy of activation 51, 883  
     enthalpy of atomization 51  
     enthalpy of chemisorption 917, (T)  
         1022  
     enthalpy of combustion 51, 52  
     enthalpy of electron gain 51, 343  
     enthalpy of formation 51  
     enthalpy of fusion 50, (T) 993  
     enthalpy of hydration 51  
     enthalpy of ionization 51, 343  
     enthalpy of mixing 51, 143  
     enthalpy of physisorption 917, (T)  
         1022  
     enthalpy of reaction 51  
     enthalpy of solution 51  
     enthalpy of sublimation 51  
     enthalpy of transition 50  
         notation 51  
     enthalpy of vaporization 49, 50, (T)  
         993  
     entropy  
         Boltzmann formula 575  
         conformational 671  
         excess 149  
         from *Q* 579  
         harmonic oscillator 576  
         internal energy 589  
         measurement 91  
         partial molar 94  
         partition function 589  
         reaction 93  
         residual 93, 609  
         statistical 575  
         statistical definition 80  
         thermodynamic definition 78  
         Third-Law 93, 575  
         two-level system 576  
     units 79  
     variation with temperature 89  
     entropy change  
         adiabatic process 80  
         heating 89  
         perfect gas expansion 79  
         phase transition 87  
         surroundings 79  
     entropy determination 91  
     entropy of activation 883  
     entropy of mixing 143  
     entropy of transition (T) 1002  
     entropy of vaporization 88, (T) 1003  
     enzyme 839, 840  
     epifluorescence 504  
     EPR 516, 549  
     EPR spectrometer 549  
     equation  
         Arrhenius 807  
         Born 102, 110  
         Born–Mayer 719  
         Clapeyron 126  
         Clausius–Clapeyron 128  
         Clausius–Mossotti 627  
         Debye 627  
         differential 971  
         diffusion 776  
         eigenvalue 261, 977  
         Einstein–Smoluchowski 782  
         Eyring 882  
         fundamental 139  
         generalized diffusion 777  
         Gibbs–Duhem 140  
         Gibbs–Helmholtz 105  
         Hartree–Fock 393  
         Karplus 528  
         Margules 162  
         Mark–Kuhn–Houwink–Sakurada  
             666  
         material balance 879  
         McConnell 552  
         Michaelis–Menten 841  
         Nernst 221  
         Nernst–Einstein 775  
         partial differential 973  
         Poisson's 168, 986  
         Roothaan 393  
         Sackur–Tetrode 580  
         secular 380, 977  
         Stern–Volmer 849  
         Stokes–Einstein 775, 878  
         Thomson 127  
         transcendental 186  
         van der Waals 17  
         van 't Hoff 156, 212, 919  
         virial 16  
         Wierl 742  
     equation of state 3  
         partition function 604  
         thermodynamic 104  
     equilibrium 35  
         approach to 804  
         Boltzmann distribution 208, 212

chemical 201  
 effect of compression 211  
 effect of temperature 211  
 mechanical 4  
 response to pressure 210  
 sedimentation 662  
 thermal 6  
 thermodynamic criterion 122  
 equilibrium bond length 363  
 equilibrium constant 203  
 contributions to 613  
 electrochemical prediction 228  
 molecular interpretation 208  
 partition function 611  
 relation between 208  
 relation to rate constant 804  
 standard cell emf 221  
 standard Gibbs energy of reaction 206  
 thermodynamic 205  
 equilibrium table 207  
 equipartition theorem 31, 247, 600  
 equivalent nuclei 526, 530  
 ER mechanism 928  
 error function 297  
 error function (T) 1009  
 ESCA 913  
 escape depth 912  
 ESR 516, 549  
 essential symmetry 699  
 ethanal pyrolysis 830  
 ethanol 396  
 ethene, MO description 387  
 Euler chain relation 68, 968  
 eutectic 191  
 eutectic halt 192  
 evanescent wave 925  
 evolution period 543  
 exact differential 58, 968  
 criterion for 103  
 excess entropy 149  
 excess function 149  
 exchange–correlation energy 395  
 exchange–correlation potential 395  
 exchange current density 937, (T) 1023  
 exchange operator 393  
 exchange process 532  
 excimer formation 846  
 exciplex laser 507  
 excited state absorption 846  
 excited state decay 848  
 exciton 304, 729  
 exciton band 730  
 excluded volume 18  
 exclusion principle 337  
 exclusion rule 464  
 exercise 53  
 exergonic 202  
 exocytosis 687  
 exothermic process 29  
 exp-6 potential 637  
 expansion coefficient 62, (T) 1002

expansion work 33  
 expectation value 267, 974  
 explosion 833  
 exponential decay 799  
 exponential function 963  
 extended Debye–Hückel law 165  
 extensive property 31, 959  
 extent of reaction 201, 794  
 extinction coefficient 432  
 extra work, see additional work 34  
 extrinsic semiconductor 726  
 eye 490  
 Eyring equation 882

## F

*f* block 342  
 face-centred cubic 716  
 face-centred unit cell 699  
 factorial 967  
 far infrared 244  
 far-field confocal microscopy 504  
 fat 53  
 fcc 716  
 FEMO 401  
 femtochemistry 892  
 femtosecond spectroscopy 893  
 Fermi calculation 790  
 Fermi contact interaction 528  
 Fermi level 725  
 fermion 309, 338  
 Fermi–Dirac distribution 726  
 ferrocene 411  
 ferromagnetism 736  
 fibre 673  
 Fick's first law of diffusion 757, 773  
 Fick's second law of diffusion 776  
 FID 535, 554  
 field 244  
 electric 244, 983  
 electromagnetic 243, 983  
 magnetic 244, 983  
 field-ionization microscopy 924  
 FIM 924  
 fine structure  
 atomic 351  
 fine structure (NMR) 524  
 finite barrier 288  
 first ionization energy 342  
 First Law of thermodynamics 32  
 first-order correction 310  
 first-order differential equation 811  
 first-order phase transition 129  
 first-order reaction 796, 798  
 first-order spectra 532  
 flash desorption 916  
 flash photolysis 793  
 flocculation 684  
 flow method 793  
 fluctuations 578  
 fluid mosaic model 687

fluorescence 492, 846  
 laser-induced 886  
 solvent effect 493  
 fluorescence lifetime 848  
 fluorescence microscopy 494  
 fluorescence quantum yield 848  
 fluorescence resonance energy transfer 852  
 flux 757  
 toward electrode 941  
 Fock operator 393  
 Fock, V. 344  
 food, energy reserves 52  
 forbidden transition 335, 435  
 force 637, 980  
 between charges 986  
 generalized 34  
 thermodynamic 772  
 force constant 290, 452  
 force field 462  
 formal potential 941  
 formaldehyde synthesis 860  
 formation 204  
 enthalpy of 51  
 formula unit 959  
 Förster theory 852, 863  
 Förster, T. 852  
 four-centred integral 395  
 four-circle diffractometer 704  
 four-helix bundle 678  
 Fourier transform 554  
 Fourier transform technique 432, 471  
 Fourier-transform NMR 533  
 fractional coverage 916  
 fractional distillation 183  
 fracture 723  
 framework representation 931  
 Franck–Condon factor 486  
 Franck–Condon principle 484, 493  
 Franklin, R. 711  
 free energy, see Gibbs energy 98  
 free expansion 34  
 free particle 277  
 free-electron molecular orbital theory 401  
 free-induction decay 535  
 freely jointed chain 75, 668  
 freeze quench method 794  
 freezing point constant 153, (T) 1004  
 freezing temperature 120  
 Frenkel exciton 729  
 frequency 244, 983  
 frequency-domain signal 536  
 frequency doubling 732  
 FRET 852  
 Freundlich isotherm 922  
 frictional coefficient 660, (T) 1017  
 Friedrich, W. 702  
 frontier orbital 388  
 FT-NMR 533  
 fuel, thermochemical properties 53  
 fuel cell 947

fuel-rich regime 834  
 fugacity 111  
 fugacity coefficient 111  
 full rotation group 411  
 functional 395, 969  
 functional derivative 395, 969  
 functional MRI 541  
 fundamental equation 103, 139  
 fundamental transition 455  
 fusion, enthalpy of 50

## G

*g* subscript 372  
*g*-value 514, 550  
 Galileo 4  
 Galvani potential 952  
 Galvani potential difference 932, 934  
 galvanic cell 216  
 working 945  
 galvanizing 949  
 gamma-ray region 244, 984  
 gas 3  
 kinetic model 9  
 gas constant 8  
 gas laser 506  
 gas laws 7  
 gas mixture 12  
 gas solubility 147  
 gas solvation 124  
 gas-sensing electrode 230  
 gauss 514  
 Gaussian function 292  
 Gaussian-type orbital 395  
 gel 682  
 gel electrophoresis 664  
 general solution 971  
 generalized diffusion equation 777  
 generalized displacement 34  
 generalized force 34  
 genomics 664  
 gerade symmetry 372  
 Gerlach, W. 307  
 Germer. 248  
 GFP 494  
 Gibbs energy 96  
 formation 100  
 maximum non-expansion work 99  
 mixing 142  
 mixing (partial miscibility) 186  
 partial molar 138  
 partition function 591  
 perfect gas 107  
 properties 105  
 reaction 100, 201  
 solvation 110  
 standard reaction 202, 220  
 surface 688  
 variation with pressure 106  
 variation with temperature 105  
 Gibbs energy of activation 883

Gibbs energy of activation (electron transfer) 903  
 Gibbs energy of formation 204  
 Gibbs energy of mixing, ideal solution 148  
 Gibbs energy of reaction 100  
 Gibbs isotherm 689  
 Gibbs, J.W. 176  
 Gibbs–Duhem equation 140  
 Gibbs–Helmholtz equation 105  
 glancing angle 704  
 glass electrode 229  
 glass transition temperature 674  
 global warming 462  
 globar 470  
 glucose oxidation 226  
 glycolysis 225  
 Gouy balance 734  
 Gouy–Chapman model 933  
 Grahame model 933  
 Graham's law of effusion 756  
 grand canonical ensemble 577  
 graphical representation 396  
 graphite structure 720  
 gravimetry 916  
 green fluorescent protein 494  
 greenhouse effect 462  
 gross selection rule 436  
 Grotian diagram 336  
 Grotthuss mechanism 766  
 group theory 404  
 GTO 395  
 Gunn oscillator 550

**H**

haematoporphyrin 861  
 hair 681  
 half-life 800, (T) 1020  
     summary 803  
 half-reaction 216  
 hamiltonian  
     core 393  
     Hückel method 388  
     hydrogen molecule-ion 368  
 hamiltonian matrix 389  
 hamiltonian operator 261  
 hard sphere packing 716  
 hard-sphere potential 637  
 harmonic motion 290  
 harmonic oscillator 291  
     energy 291  
     entropy 576  
     penetration 296  
     wavefunction 291  
 harmonic oscillator (classical) 982  
 harmonic wave 983  
 Harned cell 222  
 harpoon mechanism 875  
 Hartree, D.R. 344  
 Hartree–Fock equations 393  
 Hartree–Fock self-consistent field 344

hcp 715, 716  
 heat 29  
 heat and work equivalence of 32  
 heat at constant pressure 41  
 heat capacity 39, 247, (T) 992  
     constant pressure 45  
     constant volume 38, 39  
     contributions summary 616, 620  
     molar 45  
     partition function 601  
     phase transition 130  
     relation between 63, 69  
     relation between (perfect gas) 47  
     rotational transitions 602  
     specific 39  
     variation with temperature 46  
     vibrational contribution 602  
 heat capacity ratio 48  
 heat engine 76  
     efficiency 83  
 Heisenberg uncertainty principle 269, 272  
 Heisenberg, W. 269  
 helium 337  
     Grotian diagram 348  
 helium-neon laser 506  
 helix scattering 711  
 helix–coil transition 571, 818  
 Helmholtz energy 96  
     molecular interpretation 97  
     partition function 590  
 Helmholtz layer model 932  
 Henry, W. 145  
 Henry's law 145  
 Henry's law constant (T) 1003  
 Hermann–Mauguin system 406  
 Hermite polynomial 292  
 hermitian operator 264, 283  
 hermiticity 313  
 Hertz 244  
 Hess's law 53  
 heterogeneous catalysis 927  
     rate law 927  
 heterogeneous catalyst 839  
 heterogeneous reaction rate 795  
 heteronuclear diatomic molecule, MO description 368, 379  
 heteronuclear spin system 532  
 hexagonal unit cell 699  
 hexagonally close-packed 715  
 HF-SCP 344  
 high-energy phosphate bond 225  
 high-performance liquid chromatography 119  
 high-temperature superconductor 736  
 highest occupied molecular orbital 388  
 Hinshelwood, C.N. 820  
 HOMO 388  
 homogeneity index 654  
 homogeneous catalyst 839  
 homogenized milk 682

homonuclear diatomic molecule  
     MO description 368  
     molecular orbital diagram 375  
     VB description 363  
 homonuclear spin system 532  
 Hooke's law 673  
 HPLC 119  
 HREELS 913  
 HTSC 736  
 Hückel approximations 387  
 Hückel method 387  
 Hückel, E. 387  
 Hull, A. 703  
 Humphreys series 359  
 Hund's maximum multiplicity rule 341  
 Hush, N.S. 896  
 hybrid orbital 366  
 hybridization 366  
     hybridization schemes 368  
 hydration, enthalpy of 51  
 hydrodynamic flow 647  
 hydrodynamic radius 766  
 hydrofluorocarbon 856  
 hydrogen atom  
     bound state 326  
     energies 324  
     wavefunction 324  
 hydrogen bond 634, 677  
 hydrogen–bromine reaction 831, 860  
 hydrogen electrode 222  
 hydrogen fluoride, MO description 379, 384  
 hydrogen ion  
     conduction by 766  
     enthalpy of formation 55  
     Gibbs energy of formation 100  
     standard entropy 94  
 hydrogen molecule  
     MO description 373  
     VB description 364  
 hydrogen molecule ion 368  
 hydrogen–oxygen reaction 833  
 hydrogen peroxide decomposition 839  
 hydrogen storage 947  
 hydrogen/oxygen fuel cell 947  
 hydrogenation 929  
 hydrogenic atom 320  
 hydrogenic orbital, mean radius 330  
 hydronium ion 766  
 hydrophilic 682  
 hydrophobic 635, 682  
 hydrophobic interaction 636  
 hydrophobicity constant 635  
 hydrostatic pressure 5  
 hydrostatic stress 721  
 hyperbola 7  
 hyperfine coupling constant 551, (T) 1015  
 hyperfine structure 551

**I**

IC 495, 846  
 ice 121  
     phase diagram 121  
     residual entropy 93, 610  
     structure 121, 721  
 icosahedral group 410  
 ideal gas, see perfect gas 8  
 ideal solution 144  
     Gibbs energy of mixing 148  
 ideal–dilute solution 146  
 identity operation 405  
 IHP 933  
 immiscible liquids 184  
 impact parameter 640  
 impressed-current cathodic protection 950  
 improper rotation 406  
 incident beam flux 648  
 incongruent melting 193  
 indefinite integral 966  
 independent migration of ions 763  
 independent molecules 579  
 indicator diagram 35  
 indicator solution 768  
 indistinguishable molecules 580  
 induced dipole moment 624  
 induced fit model 840  
 induced magnetic moment 736  
 induced-dipole–induced-dipole interaction 633  
 induction period 812  
 inelastic neutron scattering 761  
 inexact differential 58  
 infectious disease kinetics 867  
 infinite temperature 567, 584  
 infrared 244  
 infrared active 454  
 infrared activity 467  
 infrared chemiluminescence 886  
 infrared inactive 454  
 infrared region 984  
 inhibition 844  
 inhomogeneous broadening 538  
 initial condition 971  
 initiation step 831  
 inner Helmholtz plane 933  
 inner potential 934  
 insulator 723  
 integral 966  
 integral protein 687  
 integrated absorption coefficient 433  
 integrated rate law 798  
     summary 803  
 integrated signal 521  
 integration 966  
 integration by parts 967  
 intensive property 959  
 interference 251, 370

interferogram 472  
 interferometer 471  
 intermolecular interaction 14  
 internal conversion 495  
 internal energy 30  
     fluid 609  
     from Q 578  
     general changes in 59  
     heat at constant volume 37  
     molecular contributions 31  
     partition function 573  
     properties 103  
     statistical 573  
 internal pressure 60  
 International System (point groups)  
     406  
 International System (units) 960  
 interstellar cloud 439  
 intersystem crossing 494  
 intrinsic semiconductor 726  
 intrinsic viscosity 665, (T) 1017  
 inverse matrix 976  
 inversion operation 406  
 inversion recovery technique 538  
 inversion symmetry 372  
 inversion temperature 66, (T) 1002  
 inverted region 899  
 iodine, metallic 178  
 ion  
     activity 163  
     Gibbs energy of formation 101  
     standard entropy 94  
 ion channel 770  
 ion mobility 765, 774  
 ion pump 770  
 ion-selective electrode 229  
 ionic atmosphere 164, 683, 769  
 ionic bond 362  
 ionic mobility (T) 1019  
 ionic radius (T) 1017  
 ionic solid 717  
 ionic strength 164  
 ionization, enthalpy of 51, 343  
 ionization energy 327, 342, (T) 1010  
     periodicity 343  
     spectroscopic measurement 325  
 ion–ion interaction (conductivity)  
     769  
 irreducible representation 415  
 irrep 415  
 ISC 494, 846  
 isenthalpic process 64  
 isobar 10, 12  
 isobaric calorimeter 41  
 isochore 10  
 isodensity surface 396  
 isoelectric focusing 665  
 isoelectric point 665  
 isolated system 29  
 isolation method 797  
 isopleth 181  
 isosteric enthalpy of adsorption 919  
 isotherm 7, 10, 15

isothermal compressibility 62, (T)  
     1002  
 isothermal expansion 79  
 isothermal Joule–Thomson  
     coefficient 65  
 isothermal reversible expansion 36  
 isotope abundance (T) 991  
 isotope separation 501  
 isotopomer 501

---

**J**

Jablonski diagram 495  
 Jeans, J. 245  
*jj*-coupling 355  
 joule 31, 961, 979  
 Joule experiment 60  
 Joule, J.P. 31, 60  
 Joule–Thomson coefficient 63, (T)  
     1002  
 Joule–Thomson effect 64

---

**K**

K-radiation 703  
 Karplus equation 528  
 Kassel form 821  
 Kassel, L.S. 821  
 Keesom interaction 632  
 kelvin 6  
 Kelvin equation 645  
 Kelvin scale 6  
 Kelvin statement 76  
 keratin 681  
 Kerr lens 733  
 Kerr medium 733  
 ket 313  
 kinetic chain length 838  
 kinetic control 815  
 kinetic energy 9, 979  
 kinetic energy density 755  
 kinetic energy operator 264  
 kinetic isotope effect 816  
 kinetic model 747  
 kinetic model of gas 9  
 kinetic pressure 609  
 kinetic theory, transport properties  
     758  
 Kirchhoff's law 56  
 klystron 550  
 KMT, see kinetic model 747  
 Knipping, P. 702  
 Knudsen method 756  
 Kohlrausch's law 762  
 Kohn–Sham equations 395  
 Koopmans' theorem 378  
 Kraft temperature 685  
 Kronecker delta 311, 975  
 krypton-ion laser 507

---

**L**

Lagrange method 582, 970  
 Laguerre polynomial 324

Lamb formula 521  
 lambda line 121, 122  
 lambda-transition 130  
 Lamé constants 743  
 lamellar micelle 685  
 laminar flow 758  
 lamp 470  
 Landau, L. 683  
 Langevin function 624  
 Langmuir isotherm 918  
 Langmuir, I. 687  
 Langmuir–Blodgett film 687  
 Langmuir–Hinshelwood mechanism  
     927  
 Laplace equation 643  
 laplacian 168, 255, 301  
 Laporte selection rule 483  
 Larmor frequency 515, 534  
 laser 732  
 laser action 496  
 laser radiation characteristics 500  
 laser-induced fluorescence 886  
 lattice energy 718  
 lattice enthalpy (T) 1018  
 lattice point 698  
 law  
     Beer–Lambert 432  
     Boyle's 7  
     Charles's 7  
     combined gas 10  
     cosines 370  
     Curie 734  
     Dalton's 13, 179  
     Debye T3 91  
     Debye–Hückel limiting 164  
     Dulong and Petit 247  
     extended Debye–Hückel 165  
     Fick's first 757, 773  
     Fick's second 776  
     First 32  
     gas 7  
     Graham's 756  
     Henry's 145  
     Hess's 53  
     Hooke's 673, 723  
     Kirchhoff's 56  
     Kohlrausch's 762  
     limiting 7  
     motion 981  
     Newton's second 981  
     Ostwald's dilution 764  
     Raoult's 144, 179  
     Rayleigh–Jeans 245  
     Second 76  
     Stefan–Boltzmann 275  
     Stokes' 775  
     Third 93  
     Wien's 275  
     Zeroth 6  
 law of cosines 370, 964  
 LCAO-MO 369, 374, 386  
     symmetry considerations 424  
 LCAO-MO (solids) 724

Le Chatelier, H. 210  
 Le Chatelier's principle 210  
 LED 732  
 LEED 914  
 legendrian 255, 301  
 Lennard-Jones parameters (T) 1016  
 Lennard-Jones potential 637  
 level  
     atomic 349  
     energies 350  
 lever rule 181  
 levitation 737  
 Lewis, G.N. 362  
 LFER 884, 899  
 LH mechanism 927  
 lifetime 437  
     rotational state 462  
 lifetime broadening 438  
 ligand-field splitting parameter 488  
 ligand-to-metal transition 489  
 light 242, 481  
 light (T) 1013  
 light-emitting diode 732  
 light harvesting 856  
 light harvesting complex 856  
 light-induced photoisomerization  
     713  
 light scattering 657, 691  
 limiting current density 942  
 limiting ionic conductivity (T) 1019  
 limiting law 7, 164  
 limiting molar conductivity 762  
 limiting transport number 768  
 Linde refrigerator 66  
 Lindemann, F. (Lord Cherwell) 820  
 Lindemann–Hinshelwood  
     mechanism 820  
 line alternation 451  
 line broadening (NMR) 532  
 line intensity 517  
 line shape 436  
 linear combination 267  
     degenerate orbital 334  
 linear combination of atomic  
     orbitals 369, 374, 386  
 linear free energy relation 884, 899  
 linear momentum, wavefunction  
     261  
 linear rotor 442, 445  
 linear-sweep voltammetry 942  
 Lineweaver–Burk plot 842  
 lipid bilayer 779  
 lipid raft model 687  
 liposome 685  
 liquid, molecular motion 761  
 liquid crystal 191, 685  
     phase diagram 192  
 liquid crystal display 189  
 liquid junction potential 218  
 liquid structure 606  
 liquid viscosity 761  
 liquid–liquid phase diagram 185  
 liquid–solid phase diagram 189

liquid-vapour boundary 127  
 lithium atom 337  
 litre 961  
 LMCT 489  
 local contribution to shielding 521  
 local density approximation 396  
 local minima 677  
 lock-and-key model 840  
 logarithm 963  
 London formula 635  
 London interaction 633  
 long-range order 606  
 longitudinal relaxation time 536  
 low energy electron diffraction 914  
 low overpotential limit 938  
 low temperature 85  
 lower critical solution temperature 186  
 lowest occupied molecular orbital 388  
 Luggin capillary 939  
 LUMO 388  
 lung 147  
 Lyman series 320  
 lyophilic 682  
 lyophobic 682  
 lyotropic liquid crystal 189  
 lyotropic mesomorph 685

**M**

macromolecule 652  
 macular pigment 490  
 Madelung constant 719  
 magic-angle spinning 549  
 magnetic field 244, 983  
 magnetic flux density 734  
 magnetic induction 514  
 magnetic levitation 737  
 magnetic moment 514, 735  
 magnetic quantum number 302  
 magnetic resonance imaging 540  
 magnetic susceptibility 522, (T) 1018  
 magnetically equivalent nuclei 530  
 magnetizability 734  
 magnetization 733  
 magnetization vector 534  
 magnetogyric ratio 514  
 MALDI 655  
 MALDI-TOF 655  
 manometer 5, 24  
 many-electron atom 320, 336  
 Marcus cross-relation 903  
 Marcus inverted region 899  
 Marcus theory 853, 896  
 Marcus, R.A. 821, 896  
 Margules equation 162  
 Mark-Kuhn-Houwink-Sakurada equation 666  
 Mars van Kreelen mechanism 930  
 MAS 549  
 mass spectrometry 655  
 material balance equation 879

matrix addition 975  
 matrix algebra 975  
 matrix diagonalization 389  
 matrix element 310, 313, 975  
 matrix-assisted laser desorption/ionization 655  
 matter flux 757  
 matter, nature of 309  
 maximum multiplicity 341  
 maximum velocity 840  
 maximum work 96  
 Maxwell construction 20  
 Maxwell distribution 750  
 Maxwell relation 104  
 Mayer  $f$ -function 605  
 MBE 728  
 MBRS 928  
 MBS 916  
 McConnell equation 552  
 mean activity coefficient 163, (T) 1004  
 mean bond enthalpy 55, (T) 1012  
 mean cubic molar mass 653  
 mean displacement 294  
 mean distance diffused 781  
 mean energies summary 616  
 mean energy 599  
 mean free path 754  
 mean molar mass 653  
 mean radius, hydrogenic orbital 330  
 mean rotational energy 600  
 mean speed 751, 752  
 mean square displacement 294  
 mean square molar mass 653  
 mean translational energy 600  
 mean value 528, 974  
 mean value theorem 967  
 mean vibrational energy 600  
 measurement, interpretation 267  
 mechanical equilibrium 4  
 mechanical property 721  
 mechanism of reaction 791  
 Meissner effect 737  
 melting, response to pressure 123  
 melting point (T) 990  
 melting temperature 119  
 melting temperature (polymer) 674  
 membrane formation 685  
 transport across 779  
 mercury photosensitization 860  
 meridional scattering 711  
 meso-tartaric acid 407  
 mesopause 854  
 mesophase 189  
 mesosphere 854  
 metal extraction 215  
 metal-to-ligand transition 489  
 metallic conductor 723  
 metallic lustre 730  
 metastable excited state 496  
 metastable phase 118  
 methane, VB description 365

method of initial rates 797  
 method of undetermined multipliers 582  
 mho 762  
 micelle 685  
 Michaelis constant 841  
 Michaelis-Menten equation 841  
 Michaelis-Menten mechanism 841  
 Michelson interferometer 432, 471  
 microcanonical ensemble 577  
 microporous material 931  
 microstructure 191  
 microwave background radiation 438  
 microwave region 244, 984  
 Mie potential 637  
 milk 682  
 Miller indices 700  
 mirror plane 406  
 Mitchell, P. 228  
 mitochondrion 225  
 mixed inhibition 845  
 mixing enthalpy of 51  
 role in equilibrium 203  
 MLCT 489  
 mmHg 4  
 MO 368  
 MO theory 362  
 mobility 765  
 mobility on surface 924  
 mode locking 499  
 mode-selective chemistry 893  
 model Bohr 360  
 Chapman 855  
 Gouy-Chapman 933  
 Grahame 933  
 Helmholtz 932  
 kinetic 9, 747  
 RRK 821, 824  
 RRKM 821  
 Zimm-Bragg 572  
 zipper 572  
 moduli 721  
 modulus 963  
 molality 140, 960  
 molar absorption coefficient 432  
 molar concentration 140, 960  
 molar conductivity 762  
 diffusion coefficient 775  
 molar heat capacity 45  
 molar magnetic susceptibility 734  
 molar mass 653  
 molar mss 959  
 molar partition function 591  
 molar polarization 627  
 molar property 959  
 molar volume 959  
 molarity 140, 960  
 mole 959  
 mole fraction 13  
 molecular beam 640, 647

molecular beam epitaxy 728  
 molecular beam scattering 916  
 molecular beams 886  
 molecular cloud 439  
 molecular collision 753  
 molecular dynamics 607, 677  
 molecular flow 647  
 molecular interaction 14  
 molecular interpretation equilibrium constant 208  
 heat and work 29  
 molecular mechanics 677  
 molecular modelling 56  
 molecular orbital 368  
 molecular orbital energy level diagram 373  
 molecular orbital theory 362, 368  
 molecular partition function 564, 591  
 molecular potential energy curve 363  
 hydrogen molecule-ion 371  
 molecular recognition 638  
 molecular scattering 641  
 molecular solid 720  
 molecular spectroscopy 430  
 molecular speed, distribution of 750  
 molecular vibration 452  
 symmetry 467  
 molecular weight, see molar mass 653, 959  
 molecularity 810  
 molten globule 198  
 moment of inertia 297, 441, 981  
 momentum flux 758  
 momentum operator 263  
 momentum representation 276  
 monochromatic source 470  
 monochromator 471  
 monoclinic unit cell 698, 699  
 monodisperse 653  
 monolayer 687  
 monomer 652  
 monopole 630  
 Monte Carlo method 607  
 Morse potential energy 455  
 most probable radius 332  
 most probable speed 752  
 mouse cell 466  
 moving boundary method 768  
 MPI 886  
 MRI 540  
 Mulliken electronegativity 380, (T) 1012  
 multi-walled nanotube 720  
 multinomial coefficient 562, 974  
 multiphoton ionization 886  
 multiphoton process 500  
 multiple quantum transition 547  
 multiplicity 353, 482  
 multipole 630  
 multipole interaction energy 630  
 mutual termination 837  
 MWNT 720

**N**

*n*-fold rotation 405  
*n*-pole 630  
*n*-type semiconductivity 727  
 NADH 225  
 NADP 857, 858  
 nanocrystal 304  
 nanodevice 690, 728  
 nanofabrication 690  
 nanoscience 288  
 nanotechnology 288, 289  
 nanotube 720, 728  
 nanowire 728  
 narcosis 147  
 natural linewidth 438  
 natural logarithm 963  
 Nd-YAG laser 731  
 near infrared region 984  
 near-field optical microscopy 504  
 nearly free-electron approximation 724  
 negative phototactic response 713  
 negative temperature 584  
 neighbouring group contribution 521, 522  
 nematic phase 189  
 neodymium laser 731  
 neon atom 341  
 Nernst diffusion layer 941  
 Nernst equation 221  
 Nernst filament 470  
 Nernst heat theorem 92  
 Nernst–Einstein equation 775  
 network solid 720  
 neutron diffraction 713  
 neutron magnetic scattering 714  
 neutron scattering 761  
 newton 961  
 Newtonian flow 758  
 Newton's second law of motion 981  
 nicotine 186  
 nitric oxide 386  
   electronic partition function 598  
   magnetism 744  
 nitrogen  
   fugacity (T) 1003  
   VB description 364  
 nitrogen fixation 385  
 nitrogen laser 507  
 nitrogen narcosis 147  
 NMR 517  
   line intensity 517  
   spectrometer 517  
 nodal plane 333  
 node 261  
 NOE 542  
 NOESY 548  
 non-Arrhenius behaviour 817  
 non-competitive inhibition 845  
 non-polarizable electrode 940  
 nonexpansion work 34  
 nonlinear phenomena 732

nonradiative decay 492  
 normal boiling point 118  
 normal freezing point 120  
 normal melting point 120  
 normal mode 461  
   group theory 467  
   infrared activity 467  
 normal transition temperature 87  
 normal Zeeman effect 360  
 normalization 258, 278, 279  
 normalization constant 257  
 notation  
   orbital 421  
 notational conventions 962  
 NSOM 504  
 nuclear *g*-factor 516  
 nuclear magnetic resonance 517  
 nuclear magneton 516  
 nuclear Overhauser effect 542  
 nuclear spin 515, (T) 1014  
   nuclear constitution 515  
   properties 516  
 nuclear spin quantum number 515  
 nuclear statistics 451  
 nucleation 645  
 nucleation step 572  
 nucleic acid 679  
 nuclide abundance (T) 991  
 nuclide mass (T) 991  
 number-average molar mass 653  
 numerical integration 972  
 nylon-66 673, 835

**O**

O branch 459  
 oblate 444  
 observable 262, 272  
   complementary 271  
 octahedral complex 488  
 octane 53  
 octupole 631  
 off-diagonal peaks 546  
 OHP 932  
 oil hydrogenation 930  
 one-component system 177  
 one-dimensional crystal 718  
 one-dimensional random walk 781  
 open system 28  
 operator 261, 272  
   angular momentum 307  
   Coulomb 393  
   exchange 393  
   hermitian 264, 283  
   kinetic energy 264  
   momentum 263  
   position 263  
   potential energy 263  
 optical activity 985  
 optical density 432  
 optical Kerr effect 733  
 optical trapping 568  
 optically active 412

orbital  
   anti-bonding 371  
   atomic 326  
   bonding 370  
   Gaussian type 395  
 orbital angular momentum 326  
   total 352  
 orbital angular momentum  
   quantum number 302  
 orbital approximation 336  
 orbital energy variation 376  
 orbital notation 421  
 order of group 416  
 order of reaction 796  
 order-disorder transition 131  
 ordinary differential equation 971  
 ore reduction 215  
 orientation polarization 626  
 Orion nebula 439  
*ortho*-hydrogen 452  
 orthogonal function 265, 282  
 orthogonality 265, 282  
 orthonormal 283  
 orthorhombic unit cell 699  
 oscillator strength 511  
 osmometry 156  
 osmosis 156  
 osmotic pressure 156  
 osmotic virial coefficient 157  
 Ostwald viscometer 666  
 Ostwald's dilution law 764  
 Otto cycle 116  
 outer Helmholtz plane 932  
 outer potential 934  
 overall order 796  
 overall partition function 599  
 Overbeek, J.T.G. 683  
 Overhauser effect spectroscopy 548  
 overlap, symmetry relation 421  
 overlap density 370  
 overlap integral 371, 375  
 overpotential 938  
 overtone 456  
 oxidant 216  
 oxidation 216  
 oxidative phosphorylation 225, 227  
 oxygen  
   electronic states 483  
   molecular properties 483  
 ozone 853

**P**

*p* band 725  
 P branch 458  
*p* orbital 332  
   real form 333  
 p-type semiconductivity 726  
 P680 857  
 P700 858  
 packing fraction 716  
 PAGE 664  
*para*-hydrogen 452  
 parabolic potential 291, 452  
 parallel band 461  
 parallel beta-sheet 678  
 parallel spins 347  
 paramagnetic 377, 734  
 paramagnetic contribution 521  
 paramagnetism 376  
 parcel (of air) 12  
 parity 372, 482  
 parity selection rule 483  
 partial charge 379  
 partial derivative 39, 968  
 partial differential equation 973  
 partial fraction 967, 803  
 partial molar entropy 94  
 partial molar Gibbs energy 138  
 partial molar quantity 136  
 partial molar volume 137  
 partial pressure 12  
 partial vapour pressure 124  
 partially miscible 149  
 partially miscible liquids 185  
   distillation 187  
 particle in a box 278  
   partition function 568  
   quantum number 280  
 particle in a sphere 304  
 particle on a ring 297  
 particle on a sphere 301  
 particular solution 971  
 partition function  
   canonical 578  
   contributions to 615  
   electronic 597  
   enthalpy 590  
   entropy 575, 589  
   equally spaced levels 563  
   equation of state 604  
   equilibrium constant 611  
   factorization 569  
   Gibbs energy 591  
   heat capacity 601  
   Helmholtz energy 590  
   internal energy 573, 589  
   molar 591  
   molecular 564, 591  
   overall 599  
   particle in a box 568  
   pressure 590  
   rate constant 882  
   rotational 592  
   second virial coefficient 605  
   standard molar 611  
 thermodynamic functions from 616  
 thermodynamic information 578  
 translational 568, 592  
 two-level system 564  
 vibrational 596  
 partition ratio 779  
 pascal 4, 961  
 Pascal's triangle 526  
 Paschen series 320

- passive transport 770  
 patch clamp technique 771  
 patch electrode 771  
 path function 57  
 Patterson synthesis 709  
 Pauli exclusion principle 337  
 Pauli principle 338, 451  
 Pauling electronegativity 379, (T)  
     1012  
 PDT 861  
 PEMD pulse sequence 543  
 penetration 286, 296, 340  
 peptide link 571, 667, 675  
 peptizing agent 682  
 perfect elastomer 673  
 perfect gas 8  
     enthalpy of mixing 143  
     entropy change 79, 87  
     entropy of mixing 143  
     equilibria 202  
     Gibbs energy 107  
     Gibbs energy of mixing 142  
     internal energy 574  
     isothermal expansion 87  
     molar volume 11  
     statistical entropy 580  
     transport properties 757, 784  
 perfect-gas temperature scale 6  
 periodicity 341  
 peripheral protein 687  
 permanent waving 681  
 permittivity 110, 627, 984, 986  
 perpendicular band 461  
 persistence length 75  
 perturbation theory 310, 313  
     polarizability 625  
     time-dependent 311  
     time-independent 310  
 Petit, A.-T. 247  
 phaeophytin 857  
 phase 117, 174  
 phase (wave) 983  
 phase boundary 118, 126  
 phase diagram 118  
     carbon dioxide 120  
     helium 121  
     ice 121  
     liquid crystal 190  
     liquid–liquid 185  
     liquid–solid 189  
     sodium and potassium 192  
     water 120, 177  
 phase problem 709  
 phase rule 176  
 phase separation 185  
 phase transition 117, 129  
     entropy of 87  
 phase-sensitive detection 550  
 phosphatidyl choline 686  
 phosphine decomposition 927  
 phospholipid 199, 686  
 phosphorescence 492, 494, 846  
 photocatalyst 861  
 photocathode 473  
 photochemical processes 845  
 photochemistry 845  
 photodeflection 502  
 photodiode 473  
 photodissociation 502  
 photodynamic therapy 860  
 photoelectric effect 250  
 photoelectron 378  
 photoelectron spectroscopy 378, 912  
 photoemission spectroscopy 912  
 photoionization 501  
 photoisomerization 502  
 photomultiplier tube 473  
 photon 250  
 photophosphorylation 858  
 photosensitization 860  
 photosphere 346  
 photosynthesis 856  
 photosystem I and II 856  
 phototactic response 713  
 photovoltaic cell detector 473  
 physical quantity 959  
 physical state 3  
 physisorption 916  
 pi bond 365  
 pi orbital 374  
 pi-bond formation energy 390  
 pi-electron bonding energy 390  
 pi pulse 538  
 pi-stacking interaction 638  
 pi<sup>\*</sup>-n transition 489  
 pi<sup>\*</sup>-pi transition 489  
 pi/2 pulse 534  
 Planck distribution 246  
 Planck, M. 246  
 Planck's constant 246  
 plane polarized 491, 984  
 plane separation 701  
 plasma 755, 925  
 plasmid 289  
 plasmon 925  
 plastic 674  
 plastic deformation 721  
 plastoquinone 858  
 PMT 473  
 Pockels cell 498  
 point dipole 629  
 point group 405  
 point group notation 408  
 Poiseuille's formula 760  
 Poisson's equation 168, 986  
 Poisson's ratio 722  
 polar bond 379  
 polar coordinates 258, 301  
 polar molecule 411, 621  
 polarizability 449, 624, (T) 1015  
     frequency dependence 626  
 polarizability volume 624, (T) 1015  
 polarizable electrode 940  
 polarization 623  
     polarization (radiation) 491  
     polarization mechanism 528, 553  
 polarization overpotential 941  
 polarized light 491  
 polaron 674  
 polyacetylene 674  
 polyacrylamide gel electrophoresis  
     664  
 polyatomic molecule  
     MO description 386  
     VB description 365  
     vibration 460  
 polychromatic source 470  
 polychromator 471  
 polydisperse 653  
 polydispersity index 654  
 polyelectrolyte 680  
 polyelectronic atom 320  
 polyene 281  
 polymer 652  
 polymerization kinetics 835  
 polymorph 121  
 polynucleotide 679  
 polypeptide 667, 677  
     helix–coil transition 818  
 polypeptide conformation transition  
     571  
 polypeptide melting 134  
 polypeptide 715  
 population 81, 561  
 population inversion 496  
 porphine 319, 429  
 position operator 263  
 positronium 359  
 postulates 272  
 potassium–bromine reaction 875  
 potential difference 987  
 potential energy 9, 979  
 potential energy operator 263  
 potential energy profile 809  
 potential energy surface 887  
 powder diffraction pattern 707  
 powder diffractometer 703  
 power 979  
     working cell 946  
 power output (laser) 498  
 power series 967  
 pre-equilibrium 815  
 pre-exponential factor 807  
 pre-exponential factor (T) 1021  
 prebiotic reactions 829  
 precession 514, 534  
 precision-specified transition 501  
 precursor state 922  
 predissociation 495  
 prefixes for units 960, 961  
 preparation period 543  
 pressure 4  
     adiabatic process 48  
     and altitude 12  
     critical 17  
     hydrostatic 5  
     internal 60, 104  
     kinetic 609  
     kinetic model 748  
 partition function 590  
 variation with reaction 792  
 pressure gauge 5  
 pressure jump 805  
 pressure units 4  
 primary absorption 846  
 primary kinetic isotope effect 816  
 primary process 845  
 primary quantum yield 847  
 primary structure 667  
 primitive unit cell 697, 699  
 principal axis 405, 444  
 principal quantum number 326  
 principle  
     Avogadro's 7  
     building-up 340  
     equal *a priori* probabilities 561  
     equipartition 247  
     exclusion 337  
     Franck–Condon 484, 896  
     Le Chatelier's 210  
     Pauli 338, 451  
     Ritz combination 321  
     uncertainty 269, 271  
     variation 380  
 principle of corresponding states 21  
 principle of equal *a priori*  
     probabilities 561  
 probability amplitude 256  
 probability density 256, 260, 974  
 probability theory 973  
 product rule 966  
 projection reconstruction 540  
 prolate 444  
 promotion 365  
 propagation step 572, 831  
 protein crystallization 712  
 protein folding problem 675  
 proteomics 664  
 proton decoupling 541  
 proton pump 772  
 pseudo first-order reaction 797  
 psi 4  
 pulse technique 533  
 pulsed beam 928  
 pulsed-field electrophoresis 664  
 pumping 496  
 pure shear 721  
 pyroelectric detector 473  
 p–n junction 727
- 
- Q**
- Q branch 458, 459  
 Q-switching 498  
 QCM 916  
 QSAR 638  
 QSSA 812  
 quadrupole 631  
 quantitative structure–activity  
     relationships 638  
 quantity calculus 7  
 quantization

angular momentum 298  
 energy 246, 260  
 space 307  
 quantum defect 347  
 quantum dot 306  
 quantum mechanics 242  
 quantum number  
   angular momentum 302  
   magnetic 302  
   nuclear spin 515  
   orbital angular momentum 302  
 particle in a box 280  
 principal 326  
 spin 308  
 spin magnetic 308  
 total angular momentum 352  
 total orbital angular momentum  
   352  
   total spin 352  
 quantum oscillation 641  
 quantum yield 859  
 quartz crystal microbalance 916  
 quartz–tungsten–halogen lamp 470  
 quasi-steady-state approximation  
   812  
 quaternary structure 668  
 quenching 849  
 quenching method 794  
 quinoline 407  
 quotient rule 966

**R**

R branch 458  
 radial distribution function  
   atom 331  
   liquid 606  
 radial wave equation 322  
 radial wavefunction 323  
 radiation, black-body 245  
 radiation source 470  
 radiative decay 492  
 radical chain reaction 830  
 radio region 244, 984  
 radius  
   hydrodynamic 766  
   most probable 332  
   Stokes 766  
 radius of gyration 658, 671, (T) 1016  
 radius of shear 683  
 radius ratio 717  
 rainbow angle 641  
 RAIRS 913  
 Ramachandran plot 676  
 Raman activity 468  
 Raman imaging 473  
 Raman spectra  
   polyatomic molecule 464  
   rotational 449  
   vibrational 459  
 Raman spectroscopy 431, 500  
 Ramsperger, H.C. 821  
 random coil 668

random walk 781  
 Raoult, F. 144  
 Raoult's law 144, 179  
 rate  
   charge transfer 934  
   surface process 922  
 rate constant (T) 1020  
   diffusion controlled 878  
   electron transfer 895  
   Kassel form 821  
   partition function 882  
   state-to-state 887  
 rate law 795  
   heterogeneous catalysis 927  
 rate of adsorption 916  
 rate of formation 794  
 rate of reaction 794  
 rate-determining step 814  
 Rayleigh radiation 431  
 Rayleigh ratio 657, 691  
 Rayleigh scattering 657  
 Rayleigh, Lord 245  
 Rayleigh–Jeans law 245  
 RDS 814  
 reaction centre 856  
 reaction coordinate 809  
 reaction enthalpy 51  
   from enthalpy of formation 55  
   measurement 212  
   temperature dependence 56  
 reaction entropy 93  
 reaction Gibbs energy 100, 201, 220  
 reaction mechanism 791  
 reaction order 796  
 reaction product imaging 886  
 reaction profile 809  
 reaction quotient 202  
 reaction rate 794  
   collision theory 809, 870  
   temperature dependence 807  
 reactive collision 886  
 reactive cross-section 871, 874  
 read gradient 540  
 real gas 8, 14  
 real-time analysis 793  
 reciprocal identity 70  
 recursion relation 292  
 redox couple 216  
 redox reaction 216  
 reduced mass 322, 752  
 reduced representation 414  
 reduced variable 21  
 reducing agent 216  
 reductant 216  
 reference electrode 939  
 reference state 54  
 refinement 710  
 reflected wave 287  
 reflection 406  
 reflection (X-ray) 704  
 reflection-absorption infrared  
   spectroscopy 913  
 reflection symmetry 483

reforming 931  
 refraction 984  
 refractive index 732, 984, (T) 1023  
 refrigeration 85  
 regular solution 162, 186  
 relation between Q and  $q$  579  
 relative mean speed 752  
 relative motion 357  
 relative permittivity 110, 627  
 relativistic effect 276  
 relaxation effect 769  
 relaxation method 805  
 relaxation time 536, 539  
 REMPI 886  
 reorganization energy 897  
 representation 414  
 representative matrix 413  
 repulsion 637  
 repulsive surface 890  
 residual entropy 93, 609  
 resolution (microscopy) 466  
 resolution (spectroscopy) 473  
 resonance 513  
 resonance condition 516  
 resonance energy transfer 851, 863  
 resonance integral 380  
 resonance Raman spectroscopy 465  
 resonant mode (laser) 497  
 resonant multiphoton ionization 886  
 respiratory chain 226  
 restoring force elastomer 673  
 resultant vector 964  
 retardation step 831  
 retinal 490, 853  
 retinol 491  
 reversible change 35  
 reversible expansion 36  
 rheology 721  
 rheometer 666  
 rhodamine 6G 508  
 rhodopsin 490  
 ribosome 840  
 ribozyme 840  
 Rice, O.K. 821  
 Rice–Herzfeld mechanism 830  
 ridge (atmospheric) 12  
 rigid rotor 442  
 Rise–Ramsperger–Kassel model 821  
 Ritz combination principles 321  
 RNA 680, 840  
 rock-salt structure 717  
 rods and cones 490  
 Röntgen, W. 702  
 root mean square deviation 270  
 root mean square distance 781  
 root mean square separation 670  
 root mean square speed 9, 749  
 rotating frame 534  
 rotating rheometer 666  
 rotational constant 443  
 rotational energy level 443  
 rotational line intensity 448  
 rotational motion 297

rotational Raman spectra 449  
 rotational spectrum 448  
 rotational structure 487  
 rotational temperature 594  
 rotational term 443  
 rotational transitions 446  
 rotor 442  
 RRK model 821, 824  
 RRKM model 821  
 rubber 694  
 ruby glass 682  
 rule  
   exclusion 464  
   gross selection 436  
   Hund's 341  
   lever 181  
   phase 176  
   Schultze–Hardy 684  
   selection 335, 356, 423  
   specific selection 436  
   Trouton's 88  
   Walden's 776  
 Runge–Kutta method 972  
 Russell–Saunders coupling 354  
 ruthenocene 411  
 Rydberg atom 360  
 Rydberg constant 320, 327  
 Rydberg molecule 401  
 Rydberg state 347  
 Rydberg, J. 320

**S**

s band 725  
 S branch 459  
 s orbital 328  
 Sackur–Tetrode equation 580  
 sacrificial anode 950  
 saddle point 888  
 SALC 422  
 salt bridge 216  
 salting-in effect 173  
 salting-out effect 173  
 SAM 690, 914  
 SATP 11  
 saturable absorber 498  
 Sayre probability relation 710  
 scalar coupling constant 524  
 scalar product 350, 514, 965  
 scanning Auger electron microscopy  
   914  
 scanning electron microscopy 254  
 scanning probe microscopy 289  
 scanning tunnelling microscopy 289  
 Scatchard equation 156  
 scattering factor 706  
 scattering theory 891  
 SCF 119, 344, 393  
 Scherrer, P. 703  
 Schoenflies system 406  
 Schrödinger equation  
   one dimensional 254  
   particle on a sphere 301

- three-dimensional 255  
 time-dependent 255  
 time-independent 254  
 vibrating molecule 453  
**Schultze–Hardy rule** 684  
**Schumann–Runge band** 510  
**screening constant (T)** 1009  
**screw axis** 910  
**screw dislocation** 910  
**scuba diving** 147  
**SDS-PAGE** 665  
**second explosion limit** 833  
**second harmonic generation** 922  
**second ionization energy** 342  
**Second Law of thermodynamics** 76  
**second radiation constant** 275  
**second virial coefficient (T)** 991  
 partition function 605  
**second-order correction** 310  
**second-order phase transition** 130  
**second-order reaction** 801  
**secondary kinetic isotope effect** 816  
**secondary process** 845  
**secondary-ion mass spectrometry**  
 913  
**secular** 380  
**secular determinant** 382  
**secular equation** 380  
**sedimentation** 660  
**sedimentation constant** 661  
**sedimentation equilibrium** 662  
**selection rule** 473  
 atom 335  
 diatomic molecules 483  
 infrared 474  
 Laporte 483  
 many-electron atom 356  
 microwave transition 474  
 molecular vibration 454  
 normal mode 467  
 parity 483  
 rotational 447  
 rotational Raman 449  
 symmetry considerations 423  
 vibrational Raman 459, 476  
 vibrations 473  
**selectivity coefficient** 230  
**selectivity filter** 771  
**self-assembled monolayer** 670  
**self-assembly** 681  
**self-consistent field** 344, 393  
**SEM** 254  
**semi-empirical method** 394  
**semiconductor** 723, 726  
**semipermeable membrane** 154  
**separation of motion** 357  
**separation of variables** 284, 358, 973  
 atom 322  
**sequencing** 668  
**SERS** 913  
**SEXAFS** 914  
**SFC** 119  
**shape-selective catalyst** 927  
**SHE** 222  
 shear 721  
 shear modulus 722  
 shell 328  
**SHG** 922  
 shielded Coulomb potential 167  
 shielded nuclear charge 339  
 shielding 339  
 electronegativity 522  
 local contribution 521  
**shielding constant**  
 atom 339  
 NMR 518  
 short-range order 606  
**SI** 960  
 side-centred unit cell 699  
**siemens** 762  
**sigma bond** 364  
**sigma electron** 370  
**sigma orbital** 369, 373  
**sign convention** 33  
**signal enhancement (NOE)** 543  
**similarity transformation** 977  
**simple distillation** 183  
**SIMS** 913  
**simultaneous equations** 976  
**single-molecule spectroscopy** 504  
**single-valued function** 259  
**single-walled nanotube** 720, 728  
**singlet state** 347  
**singlet–singlet energy transfer** 846  
**SIR model** 867  
 Slater determinant 339, 392  
**slice selection** 540  
**slip plane** 723  
**smectic phase** 189  
**smoke** 682  
**sodium D lines** 351  
**solar radiation** 463  
**solder** 191  
**solid-state NMR** 548  
**solid–liquid boundary** 126  
**solid–vapour boundary** 129  
**soliton** 674  
**solubility** 153  
**solute activity** 159  
**solution, enthalpy of** 51  
**solvation, Gibbs energy of** 110  
**solvent-accessible surface** 396  
**solvent contribution** 521, 524  
**sp hybrid** 367  
**sp<sup>2</sup> hybrid** 367  
**sp<sup>3</sup> hybrid** 366  
**space group** 405  
**space lattice** 697  
**space quantization** 307  
**spatial coherence** 497  
**specific enthalpy** 52  
**specific heat capacity** 39  
**specific selection rule** 436  
**specific volume (polymer)** 674  
**spectral regions** 244  
**spectrometer** 431, 470, 517, 549  
**spectrophotometry** 792  
**spectroscopic transition** 249  
**spectroscopy** 248, 431  
**spectrum** 249  
**speed** 980  
 distribution 749  
 drift 765, 774  
 mean 751, 752  
 most probable 752  
 relative mean 752  
 root mean square 749  
**speed of light** 243  
**sphalerite** 717  
**spherical harmonic** 302  
**spherical polar coordinates** 168, 258,  
 301  
**spherical rotor** 442  
**spin** 308  
 total 352  
**spin correlation** 341  
**spin density** 552  
**spin echo** 539  
**spin label** 554, 686  
**spin magnetic quantum number**  
 308  
**spin packet** 539  
**spin paired** 337  
**spin probe** 554  
**spin quantum number** 308  
**spin relaxation** 536  
**spin-<sup>1/2</sup> nucleus** 517  
**spin–lattice relaxation time** 536  
**spin–orbit coupling** 348  
**spin–orbit coupling constant** 350  
**spin–spin coupling** 528  
**spin–spin relaxation time** 538  
**spiral growth** 911  
**spiral ramp** 910  
**SPM** 289  
**spontaneity, criteria for** 95  
**spontaneous** 76  
**spontaneous cooling** 86  
**spontaneous emission** 434  
**SPR** 925  
**square square well** 283  
**SQUID** 735  
**stability parameter** 571  
**standard ambient temperature and**  
 pressure 11  
**standard boiling point** 118  
**standard chemical potential** 141  
**standard emf** 220  
 determination 222  
**standard enthalpy change** 49  
**standard enthalpy of formation** 54  
**standard enthalpy of fusion** 50  
**standard enthalpy of transition** 50  
**standard enthalpy of vaporization**  
 49, 50  
**standard entropy** 93  
**standard freezing point** 120  
**standard Gibbs energy of formation**  
 204  
**standard Gibbs energy of reaction**  
 100  
**standard hydrogen electrode** 222  
**standard model (stellar structure)**  
 790  
**standard molar partition function**  
 611  
**standard potential** 222, (T) 1005  
 combining 222  
 equilibrium constant 228  
**standard pressure** 4  
**standard reaction enthalpy** 51  
**standard reaction entropy** 93  
**standard reaction Gibbs energy** 202,  
 220  
**standard state** 49  
 biological 161, 209  
**standard state summary** 158  
**standard temperature and pressure**  
 11  
**star** 346  
**Stark effect** 446, 621  
**Stark modulation** 446  
**state function** 31, 57  
 entropy 82  
**state-to-state cross-section** 887  
**state-to-state dynamics** 886  
**state-to-state reaction dynamics** 501  
**statistical entropy** 81, 575  
 perfect gas 580  
**statistical thermodynamics** 560  
**statistics** 973  
**steady-state approximation** 812, 831  
**steam distillation** 184  
**Stefan–Boltzmann law** 275  
**stellar interior** 755  
**stellar structure** 346, 755, 790  
**step** 910  
**stepwise polymerization** 835  
**steric factor** 874  
**steric requirement** 873  
**Stern model** 933  
**Stern, O.** 307  
**Stern–Gerlach experiment** 307  
**Stern–Volmer equation** 849  
**Stern–Volmer plot** 850  
**steroid binding** 639  
**sticking probability** 923  
**stimulated absorption** 434  
**stimulated emission** 434, 846  
**stimulated Raman spectroscopy** 501  
**Stirling’s approximation** 563, 974  
**STM** 289  
**stoichiometric coefficient** 203  
**stoichiometric number** 203  
**Stokes formula** 765  
**Stokes radiation** 431  
**Stokes radius** 766  
**Stokes’ law** 775  
**Stokes–Einstein equation** 775, 878  
**Stokes–Einstein relation** 660  
**stopped-flow technique** 793  
**STP** 11

- strain 721  
 stratosphere 853  
 stress 721  
 strong electrolyte 762  
 strongly coupled spectra 532  
 structure factor (X-ray) 706  
 structure factor (light scattering) 657  
 structure refinement 710  
 sublimation  
     enthalpy of 51  
 sublimation vapour pressure 118  
 subshell 328  
 subshell energies 340  
 substance 959  
 substrate 840, 909  
 sulfur dioxide spectrum 484  
 Sun 754  
 supercoiled DNA 680  
 superconducting magnet 517  
 superconducting quantum interference device 735  
 superconductor 723, 736  
 supercooled 645  
 supercritical carbon dioxide 119  
 supercritical fluid 17, 118  
 supercritical fluid chromatography  
     119  
 supercritical water 119  
 superfluid 121  
 superheated 645  
 superoxide ion 385  
 superposition 267, 364  
 superradiant 507  
 supersaturated 645  
 supersonic beam 647  
 supersonic nozzle 648  
 supertwist 189  
 surface composition 688, 911  
 surface defect 910  
 surface excess 688  
 surface film balance 687  
 surface Gibbs energy 688  
 surface growth 910  
 surface plasmon resonance 925  
 surface potential 934  
 surface pressure 687  
 surface reconstruction 915  
 surface tension 642, 689, (T) 1016  
 surface-enhanced Raman scattering  
     913  
 surface-extended X-ray absorption fine structure spectroscopy  
     914  
 surfactant accumulation 689  
 surroundings 28  
     entropy change 79  
 susceptibility 522  
 sweating 53  
 SWNT 720, 728  
 symmetric rotor 442, 444  
 symmetric stretch 461  
 symmetry and degeneracy 286  
 symmetry axis 405  
 symmetry element 404  
 symmetry number 595  
 symmetry operation 404  
 symmetry species 415, 416  
 symmetry-adapted linear combination 422  
 synchrotron radiation 470, 713  
 synchrotron storage ring 470  
 system 28  
     one-component 177  
 systematic absences 707  
*Système International* 4
- 
- T**
- T*<sub>1</sub>-weighted image 540  
*T*<sub>2</sub>-weighted image 541  
 $T^3$  law 91  
 Tafel plot 939  
 Taylor expansion 967  
 Taylor series 967  
 TDS 924  
 Teller, E. 920  
 TEM 253  
 Temkin isotherm 922  
 temperature 5  
     characteristic rotational 594  
     characteristic vibrational 597  
     consolute 186  
     critical solution 186  
     Curie 736  
     Debye 248  
     Einstein 248  
     infinite 567, 584  
     Krafft 685  
     Néel 736  
     negative 584  
 temperature conversion 7  
 temperature jump 805  
 temperature scale, thermodynamic 86  
 temperature-independent paramagnetism 736  
 temperature-composition diagram 182  
 temporal coherence 497  
 tensile strength 723  
 term, atomic 321  
 term symbol  
     atom 352  
     diatomic molecules 482  
 termination step 831  
 terrace 910  
 tertiary structure 668  
 tesla 514  
 tetragonal unit cell 699  
 tetrahedral group 410  
 theorem  
     equipartition 31, 600  
     Koopmans' 378  
     Nernst heat 92  
     virial 296  
 theoretical plate 183
- theory  
     activated complex 880  
     Debye–Hückel 164, 167, 222  
     Debye–Hückel–Onsager 769  
     Förster 852  
     Marcus 896  
     transition state 880  
 thermal analysis 178, 191  
 thermal conduction 747  
 thermal conductivity 758, 759, 785  
 thermal de Broglie wavelength 570  
 thermal desorption spectroscopy 924  
 thermal equilibrium 6  
 thermal explosion 833  
 thermal motion 29  
 thermal neutrons 714  
 thermal wavelength 570  
 thermochemical equation 51  
 thermochemistry 49  
 thermodynamic data:  
     inorganic (T) 995  
     organic (T) 993  
 thermodynamic equation of state 104  
 thermodynamic equilibrium constant 205  
 thermodynamic force 772  
 thermodynamic function,  
     electrochemical determination 230  
 thermodynamic limit 577  
 thermodynamic temperature scale 6, 86  
 thermodynamics 28  
     First Law 32  
     Second Law 76  
     Third Law 93  
     Zeroth Law 6  
 thermogram 43  
 thermolysis 831  
 thermometer 6  
 thermosphere 854  
 theta-solution 659  
 theta-temperature 659  
 third explosion limit 833  
 Third Law of thermodynamics 93  
 Third-Law entropy 93, 575  
 Thomson equation 127  
 three-level laser 496  
 tie line 181  
 tight-binding approximation 724  
 time constant 801  
 time-dependent perturbation theory 311, 315  
 time-dependent Schrödinger equation 255  
 time-domain signal 536  
 time-independent perturbation theory 310, 313  
 time-independent Schrödinger equation 254  
 time-of-flight spectrometer 655  
 time-resolved spectroscopy 503
- time-resolved X-ray diffraction 713  
 TIP 736  
 titanium ion spectrum 488  
 TMS 519  
 TOF 655  
 tonne 961  
 torque 981  
 torr 4  
 Torricelli 4  
 total angular momentum 349  
 total angular momentum quantum number 352  
 total energy 979  
 total orbital angular momentum quantum number 352  
 total rate of absorption 434  
 total spin quantum number 352  
 TPD 924  
 trajectory 980  
 trajectory on surface 888  
*trans*-retinal 490  
 transcendental equation 186  
 transfer coefficient 937, (T) 1023  
 transfer RNA 680  
 transition 335  
     charge-transfer 489  
     cooperative 572  
     enthalpy of 50  
     helix-coil 571, 818  
     polypeptide conformation 571  
     spectroscopic 249  
 transition dipole interaction 729  
 transition dipole moment 312, 335, 435, 473, 484  
     symmetry considerations 424  
 transition metal 342  
 transition rate 312  
 transition state 809, 881, 888  
 transition state theory 880  
 transition temperature 87, 117  
 translational motion 277  
 transmission coefficient 881  
 transmission electron microscopy 253  
 transmission probability 287  
 transmittance 432  
 transmitted wave 287  
 transport number 768  
 transport properties 747, (T) 1018  
     kinetic theory 758  
     perfect gas 757, 784  
 transpose matrix 975  
 transverse relaxation time 537  
 trial wavefunction 380  
 triclinic unit cell 699  
 tridiagonal determinant 724  
 trigonal unit cell 699  
 trihydrogen molecule ion 429  
 triple point 86, 120  
 triplet state 494  
     vector diagram 347  
 triplet-triplet energy transfer 846  
 tRNA 680

tropopause 12, 853  
 troposphere 11, 853  
 trough (atmospheric) 12  
 Trouton's rule 88  
 tunnelling 286, 296, 817, 896  
 turnover frequency 842  
 two-dimensional box 283  
 two-dimensional electrophoresis 665  
 two-dimensional NMR 543  
 two-level system 564, 573  
 Type I and II superconductor 737

**U**

*u* subscript 372  
 ubiquitin (thermogram) 43  
 UHV 911  
 ultracentrifugation 660  
 ultracentrifuge 661  
 ultrafast techniques 892  
 ultrahigh vacuum technique 911  
 ultrapurity 192  
 ultraviolet 244  
 ultraviolet catastrophe 246  
 ultraviolet photoelectron spectroscopy 378, 913  
 ultraviolet radiation 855  
 ultraviolet region 984  
 uncertainty principle 269  
 uncompetitive inhibition 845  
 undetermined multiplier 970  
 undetermined multipliers 582  
 ungerade symmetry 372  
 uniaxial stress 721  
 unimolecular reaction 810, 820  
 unique rate of reaction 794  
 unit 959  
 unit cell 698  
 unit cell volume 743  
 unit matrix 975  
 unit vector 964  
 upper critical solution temperature 186  
 UPS 378, 912, 913  
 uranium isotope separation 502  
 urea 53  
 US standard atmosphere 12  
 UVB 855

**V**

vacuum permittivity 986  
 vacuum ultraviolet 244  
 valence band 726  
 valence bond theory 362, 363  
 van der Waals coefficients 18, (T) 992

van der Waals equation 17, 19  
 fugacity coefficient 112  
 internal pressure 105  
 van der Waals interaction 629  
 van der Waals isotherms 20  
 van der Waals loops 20  
 van der Waals molecule 641  
 van der Waals, J.D. 17  
 van't Hoff equation (equilibrium) 212  
 van't Hoff equation (osmosis) 156  
 vanishing integral 419, 423  
 vaporization  
   enthalpy of 49, 50  
   entropy of 88  
 vapour composition 179  
 vapour diffusion method 712  
 vapour pressure 17, 118  
   curved surface 645  
   decomposition 206  
   effect of applied pressure 124  
   partial 124  
   variation with composition 179  
 vapour pressure lowering 150  
 variance 176  
 variation principle 380  
 VB theory 362  
 vector 964  
 vector addition 964  
 vector algebra 964  
 vector diagram  
   parallel spins 347  
   spin paired 337  
   triplet state 347  
 vector model 308  
 vector multiplication 965  
 vector product 965  
 vector representation 300  
 velocity 980  
 velocity selector 647, 753  
 vertical transition 484  
 Verwey, E. 683  
 vibration 452  
 vibrational microscopy 466  
 vibrational modes 460  
 vibrational motion 290  
 vibrational partition function 596  
 vibrational progression 485  
 vibrational Raman spectra 459  
 vibrational term 453  
 vibrational wavenumber (T) 1013  
 vibration–rotation spectra 457  
 vibronic laser 731  
 vibronic transition 484  
 virial 609  
 virial coefficient 16  
 virial equation of state 16, 19

virial theorem 296  
 viscosity 665, 747, 758, 759, 761, 785, (T) 1019  
 diffusion coefficient 775  
 viscosity-average molar mass 653  
 visible region 984  
 vision 490  
 vitamin C 386  
 volcano curve 929  
 voltammetry 940  
 volume magnetic susceptibility 734  
 von Laue, M. 702

**W**

Walden's rule 776  
 Wannier exciton 729  
 water  
   conduction in 766  
   entropy of vaporization 89  
   phase diagram 120, 177  
   radial distribution function 606  
   residual entropy 610  
   supercritical 119  
   superfluid phase 122  
   triple point 86, 120  
   VB description 365  
   vibrations 461  
   viscosity 761  
 Watson, J. 711  
 watt 961, 979  
 wave 983  
 wave equation 983  
 wave packet 269  
 wavefunction 253, 272  
   acceptability 259  
   acceptable 272  
   antisymmetric 338  
   constraints 259  
   harmonic oscillator 291  
   hydrogen 324  
   interpretation 256  
   linear momentum 261  
 particle in a box 280  
 particle on a rectangular surface 285  
 radial 323  
 separation 322  
 trial 380  
 wavelength 244  
 wavenumber 244, 983  
 wavepacket 892  
 wave–particle duality 253  
 weak acid 763  
 weak electrolyte 763, 764  
 weather 11  
 weather map 12

weight (configuration) 562  
 weight-average molar mass 652  
 wet 644  
 white paper 658  
 wide-field epifluorescence method 504  
 Wierl equation 742  
 Wilkins, M. 711  
 wind 11, 12  
 work 29  
   additional 34, 99  
   against constant pressure 35  
   electrical 34  
   expansion 33  
   gas production 36  
   general expression 33  
   maximum 96  
   maximum non-expansion 99  
   nonexpansion 34  
   surface expansion 34  
   varieties of 34  
 work function 301  
 wrinkle, Nature's abhorrence of 777

**X**

X-ray 702  
 X-ray crystallography 711  
 X-ray diffraction 702  
 X-ray fluorescence 914  
 X-ray photoelectron spectroscopy 912  
 X-ray region 244, 984  
 xanthophyll 490  
 xenon discharge lamp 470  
 XPS 912

**Y**

yield point 723  
 Young's modulus 722

**Z**

Z-average molar mass 653  
 Zeeman effect 360  
 zeolite 931  
 zero-order reaction 796  
 zero-point energy 281, 291  
 Zeroth Law of thermodynamics 6  
 zeta potential 683  
 Zimm–Bragg model 572  
 zinc blende 717  
 zipper model 572  
 zone levelling 191  
 zone refining 190