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

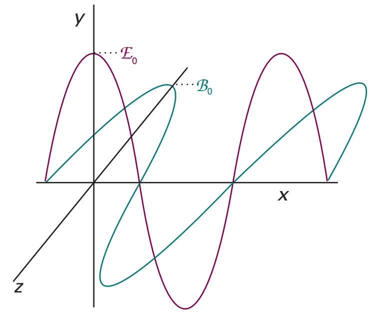

Fig. A3.7 Electromagnetic radiation consists of a wave of electric and magnetic fields perpendicular to the direction of propagation (in this case the *x*-direction), and mutually perpendicular to each other. This illustration shows a plane-polarized wave, with the electric and magnetic fields oscillating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

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

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

where λ 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 α-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.

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

	434 nm	589 nm	656 nm
$C_6H_6(l)$	1.524	1.501	1.497
$CS_2(l)$	1.675	1.628	1.618
$H_2O(l)$	1.340	1.333	1.331
$KI(s)$	1.704	1.666	1.658

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

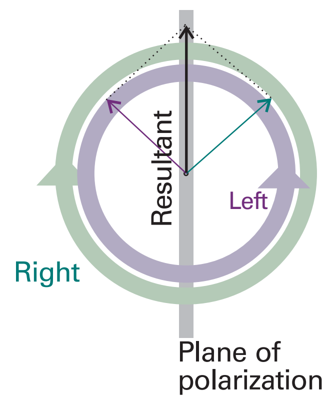

Fig. A3.8 The superposition of left and right circularly polarized light as viewed from an observer facing the oncoming beam.

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 $e \approx 1.60 \times 10^{-19}$ C. The magnitude of the charge per mole is Faraday's constant: $F = N_A e = 9.65 \times 10^4$ C mol^{-1}.

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

$$V=\frac{q_1q_2}{4\pi\varepsilon_0 r} \tag{A3.30}$$

The constant ε_0 is the **vacuum permittivity**, a fundamental constant with the value $8.85\times10^{-12}\ \mathrm{C^2\,J^{-1}\,m^{-1}}$. 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, $\boldsymbol{F}$, exerted by a charge q_1 on a second charge q_2 has magnitude

$$F=\frac{q_1q_2}{4\pi\varepsilon_0 r^2} \tag{A3.31}$$

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**, ε, 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**, ϕ:

$$V=q_1\phi \qquad \phi=\frac{q_2}{4\pi\varepsilon_0 r} \tag{A3.32}$$

The units of potential are joules per coulomb, $\mathrm{J\,C^{-1}}$, so, when φ 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:

$$1\ \mathrm{V}=1\ \mathrm{J\,C^{-1}} \tag{A3.33}$$

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

$$\phi=\phi_2+\phi_3+\cdots \tag{A3.34}$$

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

$$\nabla^2\phi=-\rho/\varepsilon_0 \tag{A3.35}$$

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 ϕ 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:

$$\mathcal{E} = -\nabla\phi \tag{A3.36}$$

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

$$1\text{ A} = 1\text{ C s}^{-1} \tag{A3.37}$$

If the current flows from a region of potential $\phi_{\rm i}$ to $\phi_{\rm f}$, through a **potential difference** $\Delta\phi = \phi_{\rm f} - \phi_{\rm i}$, 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

$$P = I\Delta\phi \tag{A3.38}$$

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

$$E = P\Delta t = I\Delta\phi\Delta t \tag{A3.39}$$

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.

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 $p^{\ominus} = 1$ 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, resived 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

	$\rho/(\mathrm{g\ cm^{-3}})$ at 293 K†	T_f/K	T_b/K
Elements			
Aluminium(s)	2.698	933.5	2740
Argon(g)	1.381	83.8	87.3
Boron(s)	2.340	2573	3931
Bromine(l)	3.123	265.9	331.9
Carbon(s, gr)	2.260	3700s	
Carbon(s, d)	3.513		
Chlorine(g)	1.507	172.2	239.2
Copper(s)	8.960	1357	2840
Fluorine(g)	1.108	53.5	85.0
Gold(s)	19.320	1338	3080
Helium(g)	0.125		4.22
Hydrogen(g)	0.071	14.0	20.3
Iodine(s)	4.930	386.7	457.5
Iron(s)	7.874	1808	3023
Krypton(g)	2.413	116.6	120.8
Lead(s)	11.350	600.6	2013
Lithium(s)	0.534	453.7	1620
Magnesium(s)	1.738	922.0	1363
Mercury(l)	13.546	234.3	629.7
Neon(g)	1.207	24.5	27.1
Nitrogen(g)	0.880	63.3	77.4
Oxygen(g)	1.140	54.8	90.2
Phosphorus(s, wh)	1.820	317.3	553
Potassium(s)	0.862	336.8	1047
Silver(s)	10.500	1235	2485
Sodium(s)	0.971	371.0	1156
Sulfur(s, α)	2.070	386.0	717.8
Uranium(s)	18.950	1406	4018
Xenon(g)	2.939	161.3	166.1
Zinc(s)	7.133	692.7	1180

	$\rho/(\mathrm{g\ cm^{-3}})$ at 293 K†	T_f/K	T_b/K
Inorganic compounds			
$CaCO_3$(s, calcite)	2.71	1612	1171d
$CuSO_4{\cdot}5H_2O$(s)	2.284	383(–H_2O)	423(–5H_2O)
HBr(g)	2.77	184.3	206.4
HCl(g)	1.187	159.0	191.1
HI(g)	2.85	222.4	237.8
H_2O(l)	0.997	273.2	373.2
D_2O(l)	1.104	277.0	374.6
NH_3(g)	0.817	195.4	238.8
KBr(s)	2.750	1003	1708
KCl(s)	1.984	1049	1773s
NaCl(s)	2.165	1074	1686
H_2SO_4(l)	1.841	283.5	611.2
Organic compounds			
Acetaldehyde, CH_3CHO(l, g)	0.788	152	293
Acetic acid, CH_3COOH(l)	1.049	289.8	391
Acetone, $(CH_3)_2CO$(l)	0.787	178	329
Aniline, $C_6H_5NH_2$(l)	1.026	267	457
Anthracene, $C_{14}H_{10}$(s)	1.243	490	615
Benzene, C_6H_6(l)	0.879	278.6	353.2
Carbon tetrachloride, CCl_4(l)	1.63	250	349.9
Chloroform, $CHCl_3$(l)	1.499	209.6	334
Ethanol, C_2H_5OH(l)	0.789	156	351.4
Formaldehyde, HCHO(g)		181	254.0
Glucose, $C_6H_{12}O_6$(s)	1.544	415	
Methane, CH_4(g)		90.6	111.6
Methanol, CH_3OH(l)	0.791	179.2	337.6
Naphthalene, $C_{10}H_8$(s)	1.145	353.4	491
Octane, C_8H_{18}(l)	0.703	216.4	398.8
Phenol, C_6H_5OH(s)	1.073	314.1	455.0
Sucrose, $C_{12}H_{22}O_{11}$(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		m/u	Abundance/%
H	^{1}H	1.0078	99.985
	^{2}H	2.0140	0.015
He	^{3}He	3.0160	0.000 13
	^{4}He	4.0026	100
Li	^{6}Li	6.0151	7.42
	^{7}Li	7.0160	92.58
B	^{10}B	10.0129	19.78
	^{11}B	11.0093	80.22
C	^{12}C	12*	98.89
	^{13}C	13.0034	1.11
N	^{14}N	14.0031	99.63
	^{15}N	15.0001	0.37
O	^{16}O	15.9949	99.76
	^{17}O	16.9991	0.037
	^{18}O	17.9992	0.204
F	^{19}F	18.9984	100
P	^{31}P	30.9738	100
S	^{32}S	31.9721	95.0
	^{33}S	32.9715	0.76
	^{34}S	33.9679	4.22
Cl	^{35}Cl	34.9688	75.53
	^{37}Cl	36.9651	24.4
Br	^{79}Br	78.9183	50.54
	^{81}Br	80.9163	49.46
I	^{127}I	126.9045	100

* Exact value.

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

	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, $C = 1200\ \mathrm{cm^6\,mol^{-1}}$.

Table 1.5 Critical constants of gases

	p_c/atm	$V_c/(\mathrm{cm^3\,mol^{-1}})$	T_c/K	Z_c	T_B/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_2S	4.484	4.34
C_2H_4	4.552	5.82	He	0.0341	2.38
C_2H_6	5.507	6.51	Kr	5.125	1.06
C_6H_6	18.57	11.93	N_2	1.352	3.87
CH_4	2.273	4.31	Ne	0.205	1.67
Cl_2	6.260	5.42	NH_3	4.169	3.71
CO	1.453	3.95	O_2	1.364	3.19
CO_2	3.610	4.29	SO_2	6.775	5.68
H_2	0.2420	2.65	Xe	4.137	5.16
H_2O	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)
Monatomic gases			
	20.78	0	0
Other gases			
Br_2	37.32	0.50	−1.26
Cl_2	37.03	0.67	−2.85
CO_2	44.22	8.79	−8.62
F_2	34.56	2.51	−3.51
H_2	27.28	3.26	0.50
I_2	37.40	0.59	−0.71
N_2	28.58	3.77	−0.50
NH_3	29.75	25.1	−1.55
O_2	29.96	4.18	−1.67
Liquids (from melting to boiling)			
$C_{10}H_8$, naphthalene	79.5	0.4075	0
I_2	80.33	0	0
H_2O	75.29	0	0
Solids			
Al	20.67	12.38	0
C (graphite)	16.86	4.77	−8.54
$C_{10}H_8$, naphthalene	−115.9	3.920×10^3	0
Cu	22.64	6.28	0
I_2	40.12	49.79	0
NcCl	45.94	16.32	0
Pb	22.13	11.72	0.96

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

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

	T_f/K	Fusion	T_b/K	Vaporization
Elements				
Ag	1234	11.30	2436	250.6
Ar	83.81	1.188	87.29	6.506
Br_2	265.9	10.57	332.4	29.45
Cl_2	172.1	6.41	239.1	20.41
F_2	53.6	0.26	85.0	3.16
H_2	13.96	0.117	20.38	0.916
He	3.5	0.021	4.22	0.084
Hg	234.3	2.292	629.7	59.30
I_2	386.8	15.52	458.4	41.80
N_2	63.15	0.719	77.35	5.586
Na	371.0	2.601	1156	98.01
O_2	54.36	0.444	90.18	6.820
Xe	161	2.30	165	12.6
K	336.4	2.35	1031	80.23
Inorganic compounds				
CCl_4	250.3	2.47	349.9	30.00
CO_2	217.0	8.33	194.6	25.23 s
CS_2	161.2	4.39	319.4	26.74
H_2O	273.15	6.008	373.15	40.656
				44.016 at 298 K
H_2S	187.6	2.377	212.8	18.67
H_2SO_4	283.5	2.56		
NH_3	195.4	5.652	239.7	23.35
Organic compounds				
CH_4	90.68	0.941	111.7	8.18
CCl_4	250.3	2.5	350	30.0
C_2H_6	89.85	2.86	184.6	14.7
C_6H_6	278.61	10.59	353.2	30.8
C_6H_{14}	178	13.08	342.1	28.85
$C_{10}H_8$	354	18.80	490.9	51.51
CH_3OH	175.2	3.16	337.2	35.27
				37.99 at 298 K
C_2H_5OH	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)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	$S_m^{\ominus}/(\mathrm{J\ K^{-1}\ mol^{-1}})$†	$C_{p,m}^{\ominus}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	$\Delta_c H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$
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
CO_2(g)	44.040	−393.51	−394.36	213.74	37.11	
Hydrocarbons						
CH_4(g), methane	16.04	−74.81	−50.72	186.26	35.31	−890
CH_3(g), methyl	15.04	+145.69	+147.92	194.2	38.70	
C_2H_2(g), ethyne	26.04	+226.73	+209.20	200.94	43.93	−1300
C_2H_4(g), ethene	28.05	+52.26	+68.15	219.56	43.56	−1411
C_2H_6(g), ethane	30.07	−84.68	−32.82	229.60	52.63	−1560
C_3H_6(g), propene	42.08	+20.42	+62.78	267.05	63.89	−2058
C_3H_6(g), cyclopropane	42.08	+53.30	+104.45	237.55	55.94	−2091
C_3H_8(g), propane	44.10	−103.85	−23.49	269.91	73.5	−2220
C_4H_8(g), 1-butene	56.11	−0.13	+71.39	305.71	85.65	−2717
C_4H_8(g), *cis*-2-butene	56.11	−6.99	+65.95	300.94	78.91	−2710
C_4H_8(g), *trans*-2-butene	56.11	−11.17	+63.06	296.59	87.82	−2707
C_4H_{10}(g), butane	58.13	−126.15	−17.03	310.23	97.45	−2878
C_5H_{12}(g), pentane	72.15	−146.44	−8.20	348.40	120.2	−3537
C_5H_{12}(l)	72.15	−173.1				
C_6H_6(l), benzene	78.12	+49.0	+124.3	173.3	136.1	−3268

Table 2.5 (Continued)

	M/(g mol^{-1})	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_f G^\ominus$/(kJ mol^{-1})	$S_m^\ominus$/(J K^{-1} mol^{-1})†	$C_{p,m}^\ominus$/(J K^{-1} mol^{-1})	$\Delta_c H^\ominus$/(kJ mol^{-1})
Hydrocarbons (Continued)						
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
Alcohols and phenols						
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
Carboxylic acids, hydroxy acids, and esters						
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
Alkanals and alkanones						
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
Sugars						
$C_6H_{12}O_6$(s), α-D-glucose	180.16	−1274				−2808
$C_6H_{12}O_6$(s), β-D-glucose	180.16	−1268	−910	212		
$C_6H_{12}O_6$(s), β-D-fructose	180.16	−1266				−2810
$C_{12}H_{22}O_{11}$(s), sucrose	342.30	−2222	−1543	360.2		−5645
Nitrogen compounds						
$CO(NH_2)_2$(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. † 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)

	$M/(\mathrm{g\,mol^{-1}})$	$\Delta_f H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	$S_m^{\ominus}/(\mathrm{J\,K^{-1}\,mol^{-1}})$†	$C_{p,m}^{\ominus}/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Aluminium (aluminum)					
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^{3+}(g)	26.98	+5483.17			
Al^{3+}(aq)	26.98	−531	−485	−321.7	
Al_2O_3(s, α)	101.96	−1675.7	−1582.3	50.92	79.04
$AlCl_3$(s)	133.24	−704.2	−628.8	110.67	91.84
Argon					
Ar(g)	39.95	0	0	154.84	20.786
Antimony					
Sb(s)	121.75	0	0	45.69	25.23
SbH_3(g)	124.77	+145.11	+147.75	232.78	41.05
Arsenic					
As(s, α)	74.92	0	0	35.1	24.64
As(g)	74.92	+302.5	+261.0	174.21	20.79
As_4(g)	299.69	+143.9	+92.4	314	
AsH_3(g)	77.95	+66.44	+68.93	222.78	38.07
Barium					
Ba(s)	137.34	0	0	62.8	28.07
Ba(g)	137.34	+180	+146	170.24	20.79
Ba^{2+}(aq)	137.34	−537.64	−560.77	+9.6	
BaO(s)	153.34	−553.5	−525.1	70.43	47.78
$BaCl_2$(s)	208.25	−858.6	−810.4	123.68	75.14
Beryllium					
Be(s)	9.01	0	0	9.50	16.44
Be(g)	9.01	+324.3	+286.6	136.27	20.79
Bismuth					
Bi(s)	208.98	0	0	56.74	25.52
Bi(g)	208.98	+207.1	+168.2	187.00	20.79
Bromine					
Br_2(l)	159.82	0	0	152.23	75.689
Br_2(g)	159.82	+30.907	+3.110	245.46	36.02
Br(g)	79.91	+111.88	+82.396	175.02	20.786
Br^-(g)	79.91	−219.07			
Br^-(aq)	79.91	−121.55	−103.96	+82.4	−141.8
HBr(g)	90.92	−36.40	−53.45	198.70	29.142
Cadmium					
Cd(s, γ)	112.40	0	0	51.76	25.98
Cd(g)	112.40	+112.01	+77.41	167.75	20.79
Cd^{2+}(aq)	112.40	−75.90	−77.612	−73.2	

Table 2.7 (Continued)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^{\ominus}/(\text{kJ mol}^{-1})$	$\Delta_f G^{\ominus}/(\text{kJ mol}^{-1})$	$S_m^{\ominus}/(\text{J K}^{-1}\text{ mol}^{-1})$†	$C_{p,m}^{\ominus}/(\text{J K}^{-1}\text{ mol}^{-1})$
Cadmium (Continued)					
$CdO(s)$	128.40	−258.2	−228.4	54.8	43.43
$CdCO_3(s)$	172.41	−750.6	−669.4	92.5	
Caesium (cesium)					
$Cs(s)$	132.91	0	0	85.23	32.17
$Cs(g)$	132.91	+76.06	+49.12	175.60	20.79
$Cs^+(aq)$	132.91	−258.28	−292.02	+133.05	−10.5
Calcium					
$Ca(s)$	40.08	0	0	41.42	25.31
$Ca(g)$	40.08	+178.2	+144.3	154.88	20.786
$Ca^{2+}(aq)$	40.08	−542.83	−553.58	−53.1	
$CaO(s)$	56.08	−635.09	−604.03	39.75	42.80
$CaCO_3(s)$ (calcite)	100.09	−1206.9	−1128.8	92.9	81.88
$CaCO_3(s)$ (aragonite)	100.09	−1207.1	−1127.8	88.7	81.25
$CaF_2(s)$	78.08	−1219.6	−1167.3	68.87	67.03
$CaCl_2(s)$	110.99	−795.8	−748.1	104.6	72.59
$CaBr_2(s)$	199.90	−682.8	−663.6	130	
Carbon (for 'organic' compounds of carbon, see Table 2.5)					
$C(s)$ (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
$C_2(g)$	24.022	+831.90	+775.89	199.42	43.21
$CO(g)$	28.011	−110.53	−137.17	197.67	29.14
$CO_2(g)$	44.010	−393.51	−394.36	213.74	37.11
$CO_2(aq)$	44.010	−413.80	−385.98	117.6	
$H_2CO_3(aq)$	62.03	−699.65	−623.08	187.4	
$HCO_3^-(aq)$	61.02	−691.99	−586.77	+91.2	
$CO_3^{2-}(aq)$	60.01	−677.14	−527.81	−56.9	
$CCl_4(l)$	153.82	−135.44	−65.21	216.40	131.75
$CS_2(l)$	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
$CN^-(aq)$	26.02	+150.6	+172.4	+94.1	
Chlorine					
$Cl_2(g)$	70.91	0	0	223.07	33.91
$Cl(g)$	35.45	+121.68	+105.68	165.20	21.840
$Cl^-(g)$	34.45	−233.13			
$Cl^-(aq)$	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
Chromium					
$Cr(s)$	52.00	0	0	23.77	23.35
$Cr(g)$	52.00	+396.6	+351.8	174.50	20.79

Table 2.7 (Continued)

	$M/(\mathrm{g\,mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\,mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$†	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Chromium (Continued)					
CrO_4^{2-}(aq)	115.99	−881.15	−727.75	+50.21	
$Cr_2O_7^{2-}$(aq)	215.99	−1490.3	−1301.1	+261.9	
Copper					
Cu(s)	63.54	0	0	33.150	24.44
Cu(g)	63.54	+338.32	+298.58	166.38	20.79
Cu^+(aq)	63.54	+71.67	+49.98	+40.6	
Cu^{2+}(aq)	63.54	+64.77	+65.49	−99.6	
Cu_2O(s)	143.08	−168.6	−146.0	93.14	63.64
CuO(s)	79.54	−157.3	−129.7	42.63	42.30
$CuSO_4$(s)	159.60	−771.36	−661.8	109	100.0
$CuSO_4\cdot H_2O$(s)	177.62	−1085.8	−918.11	146.0	134
$CuSO_4\cdot 5H_2O$(s)	249.68	−2279.7	−1879.7	300.4	280
Deuterium					
D_2(g)	4.028	0	0	144.96	29.20
HD(g)	3.022	+0.318	−1.464	143.80	29.196
D_2O(g)	20.028	−249.20	−234.54	198.34	34.27
D_2O(l)	20.028	−294.60	−243.44	75.94	84.35
HDO(g)	19.022	−245.30	−233.11	199.51	33.81
HDO(l)	19.022	−289.89	−241.86	79.29	
Fluorine					
F_2(g)	38.00	0	0	202.78	31.30
F(g)	19.00	+78.99	+61.91	158.75	22.74
F^-(aq)	19.00	−332.63	−278.79	−13.8	−106.7
HF(g)	20.01	−271.1	−273.2	173.78	29.13
Gold					
Au(s)	196.97	0	0	47.40	25.42
Au(g)	196.97	+366.1	+326.3	180.50	20.79
Helium					
He(g)	4.003	0	0	126.15	20.786
Hydrogen (see also deuterium)					
H_2(g)	2.016	0	0	130.684	28.824
H(g)	1.008	+217.97	+203.25	114.71	20.784
H^+(aq)	1.008	0	0	0	0
H^+(g)	1.008	+1536.20			
H_2O(s)	18.015			37.99	
H_2O(l)	18.015	−285.83	−237.13	69.91	75.291
H_2O(g)	18.015	−241.82	−228.57	188.83	33.58
H_2O_2(l)	34.015	−187.78	−120.35	109.6	89.1
Iodine					
I_2(s)	253.81	0	0	116.135	54.44
I_2(g)	253.81	+62.44	+19.33	260.69	36.90

Table 2.7 (Continued)

	$M/(\mathrm{g\,mol^{-1}})$	$\Delta_f H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	$S_m^{\ominus}/(\mathrm{J\,K^{-1}\,mol^{-1}})$†	$C_{p,m}^{\ominus}/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Iodine (Continued)					
I(g)	126.90	+106.84	+70.25	180.79	20.786
I^-(aq)	126.90	−55.19	−51.57	+111.3	−142.3
HI(g)	127.91	+26.48	+1.70	206.59	29.158
Iron					
Fe(s)	55.85	0	0	27.28	25.10
Fe(g)	55.85	+416.3	+370.7	180.49	25.68
Fe^{2+}(aq)	55.85	−89.1	−78.90	−137.7	
Fe^{3+}(aq)	55.85	−48.5	−4.7	−315.9	
Fe_3O_4(s) (magnetite)	231.54	−1118.4	−1015.4	146.4	143.43
Fe_2O_3(s) (haematite)	159.69	−824.2	−742.2	87.40	103.85
FeS(s, α)	87.91	−100.0	−100.4	60.29	50.54
FeS_2(s)	119.98	−178.2	−166.9	52.93	62.17
Krypton					
Kr(g)	83.80	0	0	164.08	20.786
Lead					
Pb(s)	207.19	0	0	64.81	26.44
Pb(g)	207.19	+195.0	+161.9	175.37	20.79
Pb^{2+}(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_2(s)	239.19	−277.4	−217.33	68.6	64.64
Lithium					
Li(s)	6.94	0	0	29.12	24.77
Li(g)	6.94	+159.37	+126.66	138.77	20.79
Li^+(aq)	6.94	−278.49	−293.31	+13.4	68.6
Magnesium					
Mg(s)	24.31	0	0	32.68	24.89
Mg(g)	24.31	+147.70	+113.10	148.65	20.786
Mg^{2+}(aq)	24.31	−466.85	−454.8	−138.1	
MgO(s)	40.31	−601.70	−569.43	26.94	37.15
$MgCO_3$(s)	84.32	−1095.8	−1012.1	65.7	75.52
$MgCl_2$(s)	95.22	−641.32	−591.79	89.62	71.38
Mercury					
Hg(l)	200.59	0	0	76.02	27.983
Hg(g)	200.59	+61.32	+31.82	174.96	20.786
Hg^{2+}(aq)	200.59	+171.1	+164.40	−32.2	
Hg_2^{2+}(aq)	401.18	+172.4	+153.52	+84.5	
HgO(s)	216.59	−90.83	−58.54	70.29	44.06
Hg_2Cl_2(s)	472.09	−265.22	−210.75	192.5	102
$HgCl_2$(s)	271.50	−224.3	−178.6	146.0	
HgS(s, black)	232.65	−53.6	−47.7	88.3	

Table 2.7 (Continued)

	$M/(\mathrm{g\,mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\,mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$†	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Neon					
Ne(g)	20.18	0	0	146.33	20.786
Nitrogen					
N_2(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_2O(g)	44.01	+82.05	+104.20	219.85	38.45
NO_2(g)	46.01	+33.18	+51.31	240.06	37.20
N_2O_4(g)	92.1	+9.16	+97.89	304.29	77.28
N_2O_5(s)	108.01	−43.1	+113.9	178.2	143.1
N_2O_5(g)	108.01	+11.3	+115.1	355.7	84.5
HNO_3(l)	63.01	−174.10	−80.71	155.60	109.87
HNO_3(aq)	63.01	−207.36	−111.25	146.4	−86.6
NO_3^-(aq)	62.01	−205.0	−108.74	+146.4	−86.6
NH_3(g)	17.03	−46.11	−16.45	192.45	35.06
NH_3(aq)	17.03	−80.29	−26.50	111.3	
NH_4^+(aq)	18.04	−132.51	−79.31	+113.4	79.9
NH_2OH(s)	33.03	−114.2			
HN_3(l)	43.03	+264.0	+327.3	140.6	43.68
HN_3(g)	43.03	+294.1	+328.1	238.97	98.87
N_2H_4(l)	32.05	+50.63	+149.43	121.21	139.3
NH_4NO_3(s)	80.04	−365.56	−183.87	151.08	84.1
NH_4Cl(s)	53.49	−314.43	−202.87	94.6	
Oxygen					
O_2(g)	31.999	0	0	205.138	29.355
O(g)	15.999	+249.17	+231.73	161.06	21.912
O_3(g)	47.998	+142.7	+163.2	238.93	39.20
OH^-(aq)	17.007	−229.99	−157.24	−10.75	−148.5
Phosphorus					
P(s, wh)	30.97	0	0	41.09	23.840
P(g)	30.97	+314.64	+278.25	163.19	20.786
P_2(g)	61.95	+144.3	+103.7	218.13	32.05
P_4(g)	123.90	+58.91	+24.44	279.98	67.15
PH_3(g)	34.00	+5.4	+13.4	210.23	37.11
PCl_3(g)	137.33	−287.0	−267.8	311.78	71.84
PCl_3(l)	137.33	−319.7	−272.3	217.1	
PCl_5(g)	208.24	−374.9	−305.0	364.6	112.8
PCl_5(s)	208.24	−443.5			
H_3PO_3(s)	82.00	−964.4			
H_3PO_3(aq)	82.00	−964.8			
H_3PO_4(s)	94.97	−1279.0	−1119.1	110.50	106.06
H_3PO_4(l)	94.97	−1266.9			
H_3PO_4(aq)	94.97	−1277.4	−1018.7	−222	

Table 2.7 (Continued)

	$M/(\mathrm{g\,mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\,mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$†	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Phosphorus (Continued)					
PO_4^{3-}(aq)	94.97	−1277.4	−1018.7	−221.8	
P_4O_{10}(s)	283.89	−2984.0	−2697.0	228.86	211.71
P_4O_6(s)	219.89	−1640.1			
Potassium					
K(s)	39.10	0	0	64.18	29.58
K(g)	39.10	+89.24	+60.59	160.336	20.786
K^+(g)	39.10	+514.26			
K^+(aq)	39.10	−252.38	−283.27	+102.5	21.8
KOH(s)	56.11	−424.76	−379.08	78.9	64.9
KF(s)	58.10	−576.27	−537.75	66.57	49.04
KCl(s)	74.56	−436.75	−409.14	82.59	51.30
KBr(s)	119.01	−393.80	−380.66	95.90	52.30
KI(s)	166.01	−327.90	−324.89	106.32	52.93
Silicon					
Si(s)	28.09	0	0	18.83	20.00
Si(g)	28.09	+455.6	+411.3	167.97	22.25
SiO_2(s, α)	60.09	−910.94	−856.64	41.84	44.43
Silver					
Ag(s)	107.87	0	0	42.55	25.351
Ag(g)	107.87	+284.55	+245.65	173.00	20.79
Ag^+(aq)	107.87	+105.58	+77.11	+72.68	21.8
AgBr(s)	187.78	−100.37	−96.90	107.1	52.38
AgCl(s)	143.32	−127.07	−109.79	96.2	50.79
Ag_2O(s)	231.74	−31.05	−11.20	121.3	65.86
$AgNO_3$(s)	169.88	−129.39	−33.41	140.92	93.05
Sodium					
Na(s)	22.99	0	0	51.21	28.24
Na(g)	22.99	+107.32	+76.76	153.71	20.79
Na^+(aq)	22.99	−240.12	−261.91	59.0	46.4
NaOH(s)	40.00	−425.61	−379.49	64.46	59.54
NaCl(s)	58.44	−411.15	−384.14	72.13	50.50
NaBr(s)	102.90	−361.06	−348.98	86.82	51.38
NaI(s)	149.89	−287.78	−286.06	98.53	52.09
Sulfur					
S(s, α) (rhombic)	32.06	0	0	31.80	22.64
S(s, β) (monoclinic)	32.06	+0.33	+0.1	32.6	23.6
S(g)	32.06	+278.81	+238.25	167.82	23.673
S_2(g)	64.13	+128.37	+79.30	228.18	32.47
S^{2-}(aq)	32.06	+33.1	+85.8	−14.6	
SO_2(g)	64.06	−296.83	−300.19	248.22	39.87
SO_3(g)	80.06	−395.72	−371.06	256.76	50.67

Table 2.7 (Continued)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$	$S_m^\ominus/(\mathrm{J\ K^{-1}\ mol^{-1}})$†	$C_{p,m}^\ominus/(\mathrm{J\ K^{-1}\ mol^{-1}})$
Sulfur (Continued)					
$H_2SO_4(l)$	98.08	−813.99	−690.00	156.90	138.9
$H_2SO_4(aq)$	98.08	−909.27	−744.53	20.1	−293
$SO_4^{2-}(aq)$	96.06	−909.27	−744.53	+20.1	−293
$HSO_4^-(aq)$	97.07	−887.34	−755.91	+131.8	−84
$H_2S(g)$	34.08	−20.63	−33.56	205.79	34.23
$H_2S(aq)$	34.08	−39.7	−27.83	121	
$HS^-(aq)$	33.072	−17.6	+12.08	+62.08	
$SF_6(g)$	146.05	−1209	−1105.3	291.82	97.28
Tin					
$Sn(s, \beta)$	118.69	0	0	51.55	26.99
$Sn(g)$	118.69	+302.1	+267.3	168.49	20.26
$Sn^{2+}(aq)$	118.69	−8.8	−27.2	−17	
$SnO(s)$	134.69	−285.8	−256.9	56.5	44.31
$SnO_2(s)$	150.69	−580.7	−519.6	52.3	52.59
Xenon					
$Xe(g)$	131.30	0	0	169.68	20.786
Zinc					
$Zn(s)$	65.37	0	0	41.63	25.40
$Zn(g)$	65.37	+130.73	+95.14	160.98	20.79
$Zn^{2+}(aq)$	65.37	−153.89	−147.06	−112.1	46
$ZnO(s)$	81.37	−348.28	−318.30	43.64	40.25

Source: NBS. † 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, $\Delta_{hyd}H^\ominus/(\mathrm{kJ\ mol^{-1}})$

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

Entries refer to $X^+(g) + Y^-(g) \rightarrow X^+(aq) + Y^-(aq)$.
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, $\Delta_{hyd}H^\ominus/(\mathrm{kJ\ mol^{-1}})$ at 298 K

Cations					
H^+	(−1090)	Ag^+	−464	Mg^{2+}	−1920
Li^+	−520	NH_4^+	−301	Ca^{2+}	−1650
Na^+	−405			Sr^{2+}	−1480
K^+	−321			Ba^{2+}	−1360
Rb^+	−300			Fe^{2+}	−1950
Cs^+	−277			Cu^{2+}	−2100
				Zn^{2+}	−2050
				Al^{3+}	−4690
				Fe^{3+}	−4430

Anions							
OH^-	−460						
F^-	−506	Cl^-	−364	Br^-	−337	I^-	−296

Entries refer to $X^\pm(g) \rightarrow X^\pm(aq)$ based on $H^+(g) \rightarrow H^+(aq)$; $\Delta H^\ominus = -1090\ \mathrm{kJ\ mol^{-1}}$.
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, α, and isothermal compressibilities, κ_T

	$\alpha/(10^{-4}\,K^{-1})$	$\kappa_T/(10^{-6}\,atm^{-1})$
Liquids		
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
Solids		
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(α), KL(κ_T).

Table 2.9 Inversion temperatures, normal freezing and boiling points, and Joule–Thomson coefficients at 1 atm and 298 K

	T_I/K	T_f/K	T_b/K	$\mu_{JT}/(K\,atm^{-1})$
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, $\Delta_{trs}S^{\ominus}/(J\,K^{-1}\,mol^{-1})$

	Fusion (at T_f)	Vaporization (at T_b)
Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Br_2	39.76 (at 265.9 K)	88.61 (at 332.4 K)
C_6H_6	38.00 (at 278.6 K)	87.19 (at 353.2 K)
CH_3COOH	40.4 (at 289.8 K)	61.9 (at 391.4 K)
CH_3OH	18.03 (at 175.2 K)	104.6 (at 337.2 K)
Cl_2	37.22 (at 172.1 K)	85.38 (at 239.0 K)
H_2	8.38 (at 14.0 K)	44.96 (at 20.38 K)
H_2O	22.00 (at 273.2 K)	109.0 (at 373.2 K)
H_2S	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_2	11.39 (at 63.2 K)	75.22 (at 77.4 K)
NH_3	28.93 (at 195.4 K)	97.41 (at 239.73 K)
O_2	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

	$\Delta_{vap}H^{\ominus}/(kJ\ mol^{-1})$	$\theta_b/°C$	$\Delta_{vap}S^{\ominus}/(J\ K^{-1}\ mol^{-1})$
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/atm	ϕ	p/atm	ϕ
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, $K/(kPa\ kg\ mol^{-1})$

	Water	Benzene
CH_4	7.55×10^4	44.4×10^3
CO_2	30.1×10^3	8.90×10^2
H_2	1.28×10^5	2.79×10^4
N_2	1.56×10^5	1.87×10^4
O_2	7.92×10^4	

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

	$K_f/(\mathrm{K\,kg\,mol^{-1}})$	$K_b/(\mathrm{K\,kg\,mol^{-1}})$
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

$b/b^{\ominus}$	HCl	KCl	$CaCl_2$	H_2SO_4	$LaCl_3$	$In_2(SO_4)_3$
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	$E^{\ominus}/V$	Reduction half-reaction	$E^{\ominus}/V$
Strongly oxidizing		$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16
$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	+3.0	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$F_2 + 2e^- \rightarrow 2F^-$	+2.87	$AgBr + e^- \rightarrow Ag + Br^-$	+0.07
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07	$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05	$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^+ + e^- \rightarrow Au$	+1.69	$In^+ + e^- \rightarrow In$	−0.14
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63	$AgI + e^- \rightarrow Ag + I^-$	−0.15
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	+1.60	$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51	$In^{3+} + 3e^- \rightarrow In$	−0.34
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51	$Tl^+ + e^- \rightarrow Tl$	−0.34
$Au^{3+} + 3e^- \rightarrow Au$	+1.40	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	−0.37
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.24	$In^{2+} + e^- \rightarrow In^+$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	+1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23	$In^{3+} + 2e^- \rightarrow In^+$	−0.44
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$S + 2e^- \rightarrow S^{2-}$	−0.48
$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97	$In^{3+} + e^- \rightarrow In^{2+}$	−0.49
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96	$U^{4+} + e^- \rightarrow U^{3+}$	−0.61
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86	$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	−0.81
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$V^{2+} + 2e^- \rightarrow V$	−1.19
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76	$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$	+0.62	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60	$U^{3+} + 3e^- \rightarrow U$	−1.79
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56	$Sc^{3+} + 3e^- \rightarrow Sc$	−2.09
$I_2 + 2e^- \rightarrow 2I^-$	+0.54	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36
$CU^+ + e^- \rightarrow Cu$	+0.52	$Ce^{3+} + 3e^- \rightarrow Ce$	−2.48
$I_3^- + 2e^- \rightarrow 3I^-$	+0.53	$La^{3+} + 3e^- \rightarrow La$	−2.52
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49	$Na^+ + e^- \rightarrow Na$	−2.71
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	+0.45	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40	$Sr^{2+} + 2e^- \rightarrow Sr$	−2.89
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	+0.36	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.91
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36	$Ra^{2+} + 2e^- \rightarrow Ra$	−2.92
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	$Cs^+ + e^- \rightarrow Cs$	−2.92
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27	$Rb^+ + e^- \rightarrow Rb$	−2.93
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22	$K^+ + e^- \rightarrow K$	−2.93
$Bi^{3+} + 3e^- \rightarrow Bi$	+0.20	$Li^+ + e^- \rightarrow Li$	−3.05

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

Reduction half-reaction	$E^\ominus$/V	Reduction half-reaction	$E^\ominus$/V
$Ag^+ + e^- \rightarrow Ag$	+0.80	$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98	$I_3^- + 2e^- \rightarrow 3I^-$	+0.53
$AgBr + e^- \rightarrow Ag + Br^-$	+0.0713	$In^+ + e^- \rightarrow In$	−0.14
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22	$In^{2+} + e^- \rightarrow In^+$	−0.40
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	+0.45	$In^{3+} + 2e^- \rightarrow In^+$	−0.44
$AgF + e^- \rightarrow Ag + F^-$	+0.78	$In^{3+} + 3e^- \rightarrow In$	−0.34
$AgI + e^- \rightarrow Ag + I^-$	−0.15	$In^{3+} + e^- \rightarrow In^{2+}$	−0.49
$Al^{3+} + 3e^- \rightarrow Al$	−1.66	$K^+ + e^- \rightarrow K$	−2.93
$Au^+ + e^- \rightarrow Au$	+1.69	$La^{3+} + 3e^- \rightarrow La$	−2.52
$Au^{3+} + 3e^- \rightarrow Au$	+1.40	$Li^+ + e^- \rightarrow Li$	−3.05
$Ba^{2+} + 2e^- \rightarrow Ba$	+2.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36
$Be^{2+} + 2e^- \rightarrow Be$	−1.85	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Bi^{3+} + 3e^- \rightarrow Bi$	+0.20	$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	−0.81	$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40	$Na^+ + e^- \rightarrow Na$	−2.71
$Ce^{3+} + 3e^- \rightarrow Ce$	−2.48	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	−0.80
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89	$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	+1.23	$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	+0.10
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	+0.36	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$Co^{2+} + 2e^- \rightarrow Co$	−0.28	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$O_2 + e^- \rightarrow O_2^-$	−0.56
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74	$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.24
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Cs^+ + e^- \rightarrow Cs$	−2.92	$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67
$Cu^+ + e^- \rightarrow Cu$	+0.52	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.20
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16	$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$F_2 + 2e^- \rightarrow 2F^-$	+2.87	$Ra^{2+} + 2e^- \rightarrow Ra$	−2.92
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44	$Rb^+ + e^- \rightarrow Rb$	−2.93
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04	$S + 2e^- \rightarrow S^{2-}$	−0.48
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36	$Sc^{3+} + 3e^- \rightarrow Sc$	−2.09
$2H^+ + 2e^- \rightarrow H_2$	0, by definition	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	+1.60	$Sr^{2+} + 2e^- \rightarrow Sr$	−2.89
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63	$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	−0.37
$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	+3.0	$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79	$Tl^+ + e^- \rightarrow Tl$	−0.34
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27	$U^{3+} + 3e^- \rightarrow U$	−1.79
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86	$U^{4+} + e^- \rightarrow U^{3+}$	−0.61
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92	$V^{2+} + 2e^- \rightarrow V$	−1.19
$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$	+0.62	$V^{3+} + e^- \rightarrow V^{2+}$	−0.26
		$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76

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

Acid	HA	A^-	K_a	pK_a
Hydriodic	HI	I^-	10^{11}	−11
Hydrobromic	HBr	Br^-	10^{9}	−9
Hydrochloric	HCl	Cl^-	10^{7}	−7
Sulfuric	H_2SO_4	HSO_4^-	10^{2}	−2
Perchloric*	$HClO_4$	ClO_4^-	4.0×10^{1}	−1.6
Hydronium ion	H_3O^+	H_2O	1	0.0
Oxalic	$(COOH)_2$	$HOOCCO_2^-$	5.6×10^{-2}	1.25
Sulfurous	H_2SO_3	HSO_3^-	1.4×10^{-2}	1.85
Hydrogensulfate ion	HSO_4^-	SO_4^{2-}	1.0×10^{-2}	1.99
Phosphoric	H_3PO_4	$H_2PO_4^-$	6.9×10^{-3}	2.16
Glycinium ion	$^+NH_3CH_2COOH$	NH_2CH_2COOH	4.5×10^{-3}	2.35
Hydrofluoric	HF	F^-	6.3×10^{-4}	3.20
Formic	HCOOH	HCO_2^-	1.8×10^{-4}	3.75
Hydrogenoxalate ion	$HOOCCO_2^-$	$C_2O_4^{2-}$	1.5×10^{-5}	3.81
Lactic	$CH_3CH(OH)COOH$	$CH_3CH(OH)CO_2^-$	1.4×10^{-4}	3.86
Acetic (ethanoic)	CH_3COOH	$CH_3CO_2^-$	1.4×10^{-5}	4.76
Butanoic	$CH_3CH_2CH_2COOH$	$CH_3CH_2CH_2CO_2^-$	1.5×10^{-5}	4.83
Propanoic	CH_3CH_2COOH	$CH_3CH_2CO_2^-$	1.4×10^{-5}	4.87
Anilinium ion	$C_6H_5NH_3^+$	$C_6H_5NH_2$	1.3×10^{-5}	4.87
Pyridinium ion	$C_5H_5NH^+$	C_6H_5N	5.9×10^{-6}	5.23
Carbonic	H_2CO_3	HCO_3^-	4.5×10^{-7}	6.35
Hydrosulfuric	H_2S	HS^-	8.9×10^{-8}	7.05
Dihydrogenphosphate ion	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Hypochlorous	HClO	ClO^-	4.0×10^{-8}	7.40
Hydrazinium ion	$NH_2NH_3^+$	NH_2NH_2	8×10^{-9}	8.1
Hypobromous	HBrO	BrO^-	2.8×10^{-9}	8.55
Hydrocyanic	HCN	CN^-	6.2×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Boric*	$B(OH)_3$	$B(OH)_4^-$	5.4×10^{-10}	9.27
Trimethylammonium ion	$(CH_3)_3NH^+$	$(CH_3)_3N$	1.6×10^{-10}	9.80
Phenol	C_6H_5OH	$C_6H_5O^-$	1.0×10^{-10}	9.99
Hydrogencarbonate ion	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.33
Hypoiodous	HIO	IO^-	3×10^{-11}	10.5
Ethylammonium ion	$CH_3CH_2NH_3^+$	$CH_3CH_2NH_2$	2.2×10^{-11}	10.65
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.2×10^{-11}	10.66
Dimethylammonium ion	$(CH_3)_2NH_2^+$	$(CH_3)_2NH$	1.9×10^{-11}	10.73
Triethylammonium ion	$(CH_3CH_2)_3NH^+$	$(CH_3CH_2)_3N$	1.8×10^{-11}	10.75
Diethylammonium ion	$(CH_3CH_2)_2NH_2^+$	$(CH_3CH_2)_2NH$	1.4×10^{-11}	10.84
Hydrogenarsenate ion	$HAsO_4^{2-}$	AsO_4^{3-}	5.1×10^{-12}	11.29
Hydrogenphosphate ion	HPO_4^{2-}	PO_4^{3-}	4.8×10^{-13}	12.32
Hydrogensulfide ion	HS^-	S^{2-}	1.0×10^{-19}	19.00

* At 293 K.

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

Acid	HA	A^-	K_a	pK_a
Acetic (ethanoic)	CH_3COOH	$CH_3CO_2^-$	1.4×10^{-5}	4.76
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Anilinium ion	$C_6H_5NH_3^+$	$C_6H_5NH_2$	1.3×10^{-5}	4.87
Boric*	$B(OH)_3$	$B(OH)_4^-$	5.4×10^{-10}	9.27
Butanoic	$CH_3CH_2CH_2COOH$	$CH_3CH_2CH_2CO_2^-$	1.5×10^{-5}	4.83
Carbonic	H_2CO_3	HCO_3^-	4.5×10^{-7}	6.35
Diethylammonium ion	$(CH_3CH_2)_2NH_2^+$	$(CH_3CH_2)_2NH$	1.4×10^{-11}	10.84
Dihydrogenphosphate ion	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Dimethylammonium ion	$(CH_3)_2NH_2^+$	$(CH_3)_2NH$	1.9×10^{-11}	10.73
Ethylammonium ion	$CH_3CH_2NH_3^+$	$CH_3CH_2NH_2$	2.2×10^{-11}	10.65
Formic	$HCOOH$	HCO_2^-	1.8×10^{-4}	3.75
Glycinium ion	$^+NH_3CH_2COOH$	NH_2CH_2COOH	4.5×10^{-3}	2.35
Hydrazinium ion	$NH_2NH_3^+$	NH_2NH_2	8×10^{-9}	8.1
Hydriodic	HI	I^-	10^{11}	−11
Hydrobromic	HBr	Br^-	10^9	−9
Hydrochloric	HCl	Cl^-	10^7	−7
Hydrocyanic	HCN	CN^-	6.2×10^{-10}	9.21
Hydrofluoric	HF	F^-	6.3×10^{-4}	3.20
Hydrogenarsenate ion	$HAsO_4^{2-}$	AsO_4^{3-}	5.1×10^{-12}	11.29
Hydrogencarbonate ion	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.33
Hydrogenoxalate ion	$HOOCCO_2^-$	$C_2O_4^{2-}$	1.5×10^{-5}	3.81
Hydrogenphosphate ion	HPO_4^{2-}	PO_4^{3-}	4.8×10^{-13}	12.32
Hydrogensulfate ion	HSO_4^-	SO_4^{2-}	1.0×10^{-2}	1.99
Hydrogensulfide ion	HS^-	S^{2-}	1.0×10^{-19}	19.00
Hydronium ion	H_3O^+	H_2O	1	0.0
Hydrosulfuric	H_2S	HS^-	8.9×10^{-8}	7.05
Hypobromous	$HBrO$	BrO^-	2.8×10^{-9}	8.55
Hypochlorous	$HClO$	ClO^-	4.0×10^{-8}	7.40
Hypoiodous	HIO	IO^-	3×10^{-11}	10.5
Lactic	$CH_3CH(OH)COOH$	$CH_3CH(OH)CO_2^-$	1.4×10^{-4}	3.86
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.2×10^{-11}	10.66
Oxalic	$(COOH)_2$	$HOOCCO_2^-$	5.6×10^{-2}	1.25
Perchloric*	$HClO_4$	ClO_4^-	4.0×10^1	−1.6
Phenol	C_6H_5OH	$C_6H_5O^-$	1.0×10^{-10}	9.99
Phosphoric	H_3PO_4	$H_2PO_4^-$	6.9×10^{-3}	2.16
Propanoic	CH_3CH_2COOH	$CH_3CH_2CO_2^-$	1.4×10^{-5}	4.87
Pyridinim ion	$C_5H_5NH^+$	C_6H_5N	5.9×10^{-6}	5.23
Sulfuric	H_2SO_4	HSO_4^-	10^2	−2
Sulfurous	H_2SO_3	HSO_3^-	1.4×10^{-2}	1.85
Triethylammonium ion	$(CH_3CH_2)_3NH^+$	$(CH_3CH_2)_3N$	1.8×10^{-11}	10.75
Trimethylammonium ion	$(CH_3)_3NH^+$	$(CH_3)_3N$	1.6×10^{-10}	9.80

* At 293 K.

Table 9.2 The error function

z	erf z	z	erf z
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
1*s*	1							1.6875
	Li	Be	B	C	N	O	F	Ne
1*s*	2.6906	3.6848	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
2*s*	1.2792	1.9120	2.5762	3.2166	3.8474	4.4916	5.1276	5.7584
2*p*			2.4214	3.1358	3.8340	4.4532	5.1000	5.7584
	Na	Mg	Al	Si	P	S	Cl	Ar
1*s*	10.6259	11.6089	12.5910	13.5745	14.5578	15.5409	16.5239	17.5075
2*s*	6.5714	7.3920	8.3736	9.0200	9.8250	10.6288	11.4304	12.2304
2*p*	6.8018	7.8258	8.9634	9.9450	10.9612	11.9770	12.9932	14.0082
3*s*	2.5074	3.3075	4.1172	4.9032	5.6418	6.3669	7.0683	7.7568
3*p*			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, $I/(\mathrm{kJ\ mol^{-1}})$

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

Data: E.

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

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

Data: E.

Table 11.2 Bond lengths, R_e/pm

(a) Bond lengths in specific molecules

Br_2	228.3
Cl_2	198.75
CO	112.81
F_2	141.78
H_2^+	106
H_2	74.138
HBr	141.44
HCl	127.45
HF	91.680
HI	160.92
N_2	109.76
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, $\Delta H^{\ominus}$(A—B)/(kJ mol^{-1}) at 298 K

Diatomic 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_3	435	H—NH_2	460	H—OH	492	H—C_6H_5	469
H_3C—CH_3	368	H_2C=CH_2	720	HC≡CH	962		
HO—CH_3	377	Cl—CH_3	352	Br—CH_3	293	I—CH_3	237
O=CO	531	HO—OH	213	O_2N—NO_2	54		

Data: HCP, KL.

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

	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)	163(i)								
		613(ii)	409(ii)								
		890(iii)	946(iii)								
O	463	360(i)	157	146(i)							
		743(ii)		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

	$\tilde{\nu}_0$/cm^{-1}	θ_V/K	B/cm^{-1}	θ_R/K	r/pm	k/(N m^{-1})	D/(kJ mol^{-1})	σ
$^1H_2^+$	2321.8	3341	29.8	42.9	106	160	255.8	2
$^1H_2$	4400.39	6332	60.864	87.6	74.138	574.9	432.1	2
$^2H_2$	3118.46	4487	30.442	43.8	74.154	577.0	439.6	2
$^1H^{19}F$	4138.32	5955	20.956	30.2	91.680	965.7	564.4	1
$^1H^{35}Cl$	2990.95	4304	10.593	15.2	127.45	516.3	427.7	1
$^1H^{81}Br$	2648.98	3812	8.465	12.2	141.44	411.5	362.7	1
$^1H^{127}I$	2308.09	3321	6.511	9.37	160.92	313.8	294.9	1
$^{14}N_2$	2358.07	3393	1.9987	2.88	109.76	2293.8	941.7	2
$^{16}O_2$	1580.36	2274	1.4457	2.08	120.75	1176.8	493.5	2
$^{19}F_2$	891.8	1283	0.8828	1.27	141.78	445.1	154.4	2
$^{35}Cl_2$	559.71	805	0.2441	0.351	198.75	322.7	239.3	2
$^{12}C^{16}O$	2170.21	3122	1.9313	2.78	112.81	1903.17	1071.8	1
$^{79}Br^{81}Br$	323.2	465	0.0809	10.116	283.3	245.9	190.2	1

Data: AIP.

Table 13.3 Typical vibrational wavenumbers, $\tilde{\nu}$/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
CO_3^{2-}	1410–1450
NO_3^-	1350–1420
NO_2^-	1230–1250
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	λ/nm	ν/(10^{14} Hz)	$\tilde{\nu}$/(10^4 cm^{-1})	E/eV	E/(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	$\tilde{\nu}_{max}/(10^4\ cm^{-1})$	λ_{max}/nm	$\varepsilon_{max}/(dm^3\ mol^{-1}\ cm^{-1})$
C=C ($\pi^* \leftarrow \pi$)	6.10	163	1.5×10^4
	5.73	174	5.5×10^3
C=O ($\pi^* \leftarrow n$)	3.7–3.5	270–290	10–20
—N=N—	2.9	350	15
	>3.9	<260	Strong
$-NO_2$	3.6	280	10
	4.8	210	1.0×10^4
C_6H_5-	3.9	255	200
	5.0	200	6.3×10^3
	5.5	180	1.0×10^5
$[Cu(OH_2)_6]^{2+}$(aq)	1.2	810	10
$[Cu(NH_3)_4]^{2+}$(aq)	1.7	600	50
H_2O ($\pi^* \leftarrow n$)	6.0	167	7.0×10^3

Table 15.2 Nuclear spin properties

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

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

Table 15.3 Hyperfine coupling constants for atoms, a/mT

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

	$\mu/(10^{-30}$ C m)	μ/D	$\alpha/(10^{-40}$ J^{-1} C^{2} m^{2})	$\alpha'/(10^{-30}$ m^{3})
Ar	0	0	1.66	1.85
C_2H_5OH	5.64	1.69		
$C_6H_5CH_3$	1.20	0.36		
C_6H_6	0	0	10.4	11.6
CCl_4	0	0	10.3	11.7
CH_2Cl_2	5.24	1.57	6.80	7.57
CH_3Cl	6.24	1.87	4.53	5.04
CH_3OH	5.70	1.71	3.23	3.59
CH_4	0	0	2.60	2.89
$CHCl_3$	3.37	1.01	8.50	9.46
CO	0.390	0.117	1.98	2.20
CO_2	0	0	2.63	2.93
H_2	0	0	0.819	0.911
H_2O	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
N_2	0	0	1.77	1.97
NH_3	4.90	1.47	2.22	2.47
1,2-$C_6H_4(CH_3)_2$	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

	(ε/k)/K	r_0/pm
Ar	111.84	362.3
C_2H_2	209.11	463.5
C_2H_4	200.78	458.9
C_2H_6	216.12	478.2
C_6H_6	377.46	617.4
CCl_4	378.86	624.1
Cl_2	296.27	448.5
CO_2	201.71	444.4
F_2	104.29	357.1
Kr	154.87	389.5
N_2	91.85	391.9
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

	$\gamma/(\mathrm{mN\ m^{-1}})$
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

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

	$M/(\mathrm{kg\ mol^{-1}})$	$D/(10^{-10}\ \mathrm{m^2\ s^{-1}})$
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	θ/°C	$K/(10^{-3}\ \mathrm{cm^3\ g^{-1}})$	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 + $HSCH_2CH_2OH$		7.16	0.66

† The θ 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/pm)†

Li^+(4)	Be^{2+}(4)	B^{3+}(4)	N^{3-}	O^{2-}(6)	F^-(6)
59	27	12	171	140	133
Na^+(6)	Mg^{2+}(6)	Al^{3+}(6)	P^{3-}	S^{2-}(6)	Cl^-(6)
102	72	53	212	184	181
K^+(6)	Ca^{2+}(6)	Ga^{3+}(6)	As^{3-}(6)	Se^{2-}(6)	Br^-(6)
138	100	62	222	198	196
Rb^+(6)	Sr^{2+}(6)	In^{3+}(6)		Te^{2-}(6)	I^-(6)
149	116	79		221	220
Cs^+(6)	Ba^{2+}(6)	Tl^{3+}(6)			
167	136	88			

***d*-block elements (high-spin ions)**

Sc^{3+}(6)	Ti^{4+}(6)	Cr^{3+}(6)	Mn^{3+}(6)	Fe^{2+}(6)	Co^{3+}(6)	Cu^{2+}(6)	Zn^{2+}(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, $\Delta H_L^{\ominus}/(\text{kJ mol}^{-1})$

	F	Cl	Br	I
Halides				
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		

Oxides							
MgO	3850	CaO	3461	SrO	3283	BaO	3114
Sulfides							
MgS	3406	CaS	3119	SrS	2974	BaS	2832

Entries refer to $MX(s) \rightarrow M^+(g) + X^-(g)$.
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
$CuSO_4\cdot 5H_2O(s)$	+176	+192
$MnSO_4\cdot 4H_2O(s)$	+2640	$+2.79\times 10^3$
$NiSO_4\cdot 7H_2O(s)$	+416	+600
$FeSO_4(NH_4)_2SO_4\cdot 6H_2O(s)$	+755	$+1.51\times 10^3$
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, σ/nm^2

Ar	0.36
C_2H_4	0.64
C_6H_6	0.88
CH_4	0.46
Cl_2	0.93
CO_2	0.52
H_2	0.27
He	0.21
N_2	0.43
Ne	0.24
O_2	0.40
SO_2	0.58

Data: KL.

Table 21.2 Transport properties of gases at 1 atm

	$\kappa/(\text{J K}^{-1}\ \text{m}^{-1}\ \text{s}^{-1})$	$\eta/\mu\text{P}$	
	273 K	273 K	293 K
Air	0.0241	173	182
Ar	0.0163	210	223
C_2H_4	0.0164	97	103
CH_4	0.0302	103	110
Cl_2	0.079	123	132
CO_2	0.0145	136	147
H_2	0.1682	84	88
He	0.1442	187	196
Kr	0.0087	234	250
N_2	0.0240	166	176
Ne	0.0465	298	313
O_2	0.0245	195	204
Xe	0.0052	212	228

Data: KL.

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

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

$$\log(\eta_{20}/\eta) = A/B,$$
$$A = 1.370\,23(t-20) + 8.36\times10^{-4}(t-20)^2$$
$$B = 109 + t \qquad t = \theta/°\mathrm{C}$$

Convert $\mathrm{kg\ m^{-1}\ s^{-1}}$ to centipoise (cP) by multiplying by 10^3 (so $\eta \approx 1$ cP for water).
Data: AIP, KL.

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

Cations		Anions	
Ba^{2+}	12.72	Br^-	7.81
Ca^{2+}	11.90	$CH_3CO_2^-$	4.09
Cs^+	7.72	Cl^-	7.635
Cu^{2+}	10.72	ClO_4^-	6.73
H^+	34.96	CO_3^{2-}	13.86
K^+	7.350	$(CO_2)_2^{2-}$	14.82
Li^+	3.87	F^-	5.54
Mg^{2+}	10.60	$[Fe(CN)_6]^{3-}$	30.27
Na^+	5.010	$[Fe(CN)_6]^{4-}$	44.20
$[N(C_2H_5)_4]^+$	3.26	HCO_2^-	5.46
$[N(CH_3)_4]^+$	4.49	I^-	7.68
NH_4^+	7.35	NO_3^-	7.146
Rb^+	7.78	OH^-	19.91
Sr^{2+}	11.89	SO_4^{2-}	16.00
Zn^{2+}	10.56		

Data: KL, RS.

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

Cations		Anions	
Ag^+	6.24	Br^-	8.09
Ca^{2+}	6.17	$CH_3CO_2^-$	4.24
Cu^{2+}	5.56	Cl^-	7.91
H^+	36.23	CO_3^{2-}	7.46
K^+	7.62	F^-	5.70
Li^+	4.01	$[Fe(CN)_6]^{3-}$	10.5
Na^+	5.19	$[Fe(CN)_6]^{4-}$	11.4
NH_4^+	7.63	I^-	7.96
$[N(CH_3)_4]^+$	4.65	NO_3^-	7.40
Rb^+	7.92	OH^-	20.64
Zn^{2+}	5.47	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	$A/(\mathrm{mS\ m^2\ mol^{-1}}/(\mathrm{mol\ dm^{-3}})^{1/2})$	$B/(\mathrm{mol\ dm^{-3}})^{-1/2}$
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, $D/(10^{-9}\ m^2\ s^{-1})$

Molecules in liquids				Ions in water			
I_2 in hexane	4.05	H_2 in $CCl_4(l)$	9.75	K^+	1.96	Br^-	2.08
in benzene	2.13	N_2 in $CCl_4(l)$	3.42	H^+	9.31	Cl^-	2.03
CCl_4 in heptane	3.17	O_2 in $CCl_4(l)$	3.82	Li^+	1.03	F^-	1.46
Glycine in water	1.055	Ar in $CCl_4(l)$	3.63	Na^+	1.33	I^-	2.05
Dextrose in water	0.673	CH_4 in $CCl_4(l)$	2.89			OH^-	5.03
Sucrose in water	0.5216	H_2O in water	2.26				
		CH_3OH in water	1.58				
		C_2H_5OH 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	θ/°C	k/s^{-1}	$t_{1/2}$
$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$	g	25	3.38×10^{-5}	5.70 h
	$HNO_3(l)$	25	1.47×10^{-6}	131 h
	$Br_2(l)$	25	4.27×10^{-5}	4.51 h
$C_2H_6 \rightarrow 2\ CH_3$	g	700	5.36×10^{-4}	21.6 min
Cyclopropane $\rightarrow$ propene	g	500	6.71×10^{-4}	17.2 min
$CH_3N_2CH_3 \rightarrow C_2H_6 + N_2$	g	327	3.4×10^{-4}	34 min
Sucrose $\rightarrow$ glucose + fructose	$aq(H^+)$	25	6.0×10^{-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	θ/°C	$k/(dm^3\ mol^{-1}\ s^{-1})$
$2\ NOBr \rightarrow 2\ NO + Br_2$	g	10	0.80
$2\ NO_2 \rightarrow 2\ NO + O_2$	g	300	0.54
$H_2 + I_2 \rightarrow 2\ HI$	g	400	2.42×10^{-2}
$D_2 + HCl \rightarrow DH + DCl$	g	600	0.141
$2\ I \rightarrow I_2$	g	23	7×10^9
	hexane	50	1.8×10^{10}
$CH_3Cl + CH_3O^-$	methanol	20	2.29×10^{-6}
$CH_3Br + CH_3O^-$	methanol	20	9.23×10^{-6}
$H^+ + OH^- \rightarrow H_2O$	water	25	1.35×10^{11}
	ice	−10	8.6×10^{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/s^{-1}	$E_a/(\text{kJ mol}^{-1})$
Cyclopropane → propene	1.58×10^{15}	272
$CH_3NC \rightarrow CH_3CN$	3.98×10^{13}	160
cis-CHD=CHD → *trans*-CHD=CHD	3.16×10^{12}	256
Cyclobutane → $2\ C_2H_4$	3.98×10^{13}	261
$C_2H_5I \rightarrow C_2H_4 + HI$	2.51×10^{17}	209
$C_2H_6 \rightarrow 2\ CH_3$	2.51×10^{7}	384
$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$	4.94×10^{13}	103
$N_2O \rightarrow N_2 + O$	7.94×10^{11}	250
$C_2H_5 \rightarrow C_2H_4 + H$	1.0×10^{13}	167

Second-order, gas-phase	$A/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
$O + N_2 \rightarrow NO + N$	1×10^{11}	315
$OH + H_2 \rightarrow H_2O + H$	8×10^{10}	42
$Cl + H_2 \rightarrow HCl + H$	8×10^{10}	23
$2\ CH_3 \rightarrow C_2H_6$	2×10^{10}	ca. 0
$NO + Cl_2 \rightarrow NOCl + Cl$	4.0×10^{9}	85
$SO + O_2 \rightarrow SO_2 + O$	3×10^{8}	27
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	2×10^{8}	44
$C_6H_5 + H_2 \rightarrow C_6H_6 + H$	1×10^{8}	ca. 25

Second-order, solution	$A/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
$C_2H_5ONa + CH_3I$ in ethanol	2.42×10^{11}	81.6
$C_2H_5Br + OH^-$ in water	4.30×10^{11}	89.5
$C_2H_5I + C_2H_5O^-$ in ethanol	1.49×10^{11}	86.6
$CH_3I + C_2H_5O^-$ in ethanol	2.42×10^{11}	81.6
$C_2H_5Br + OH^-$ in ethanol	4.30×10^{11}	89.5
$CO_2 + OH^-$ in water	1.5×10^{10}	38
$CH_3I + S_2O_3^{2-}$ in water	2.19×10^{12}	78.7
Sucrose + H_2O in acidic water	1.50×10^{15}	107.9
$(CH_3)_3CCl$ solvolysis		
in water	7.1×10^{16}	100
in methanol	2.3×10^{13}	107
in ethanol	3.0×10^{13}	112
in acetic acid	4.3×10^{13}	111
in chloroform	1.4×10^{4}	45
$C_6H_5NH_2 + C_6H_5COCH_2Br$		
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

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

C_2H_2	−38	H_2	−84
C_2H_4	−34	H_2O	−59
CH_4	−21	N_2	−21
Cl_2	−36	NH_3	−38
CO	−25	O_2	−21
CO_2	−25		

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

Table 25.2 Enthalpies of chemisorption, $\Delta_{ad}H^{\ominus}/(kJ\ mol^{-1})$

Adsorbate	Adsorbent (substrate)											
	Ti	Ta	Nb	W	Cr	Mo	Mn	Fe	Co	Ni	Rh	Pt
H_2		−188			−188	−167	−71	−134			−117	
N_2		−586						−293				
O_2						−720					−494	−293
CO	−640							−192	−176			
CO_2	−682	−703	−552	−456	−339	−372	−222	−225	−146	−184		
NH_3				−301				−188		−155		
C_2H_4		−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	$E_a/(\text{kJ mol}^{-1})$
$2\,HI \rightarrow H_2 + I_2$	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_2(g)	144

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

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
KI(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.

Table 25.6 Exchange current densities and transfer coefficients at 298 K

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

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

Character tables

The groups C_1, C_s, C_i

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

$C_s = C_h$ (m)	E	σ_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_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, xz, yz$
A_u	1	−1	x, y, z	

The groups C_{nv}

C_{2v}, $2mm$	E	C_2	σ_v	σ'_v	$h=4$	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	−1	−1	xy	R_z
B_1	1	−1	1	−1	x, xz	R_y
B_2	1	−1	−1	1	y, yz	R_x

C_{3v}, $3m$	E	$2C_3$	$3\sigma_v$	$h=6$	
A_1	1	1	1	z, z^2, x^2+y^2	
A_2	1	1	−1		R_z
E	2	−1	0	$(x, y), (xy, x^2-y^2)$ (xz, yz)	(R_x, R_y)

C_{4v}, $4mm$	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$	$h=8$	
A_1	1	1	1	1	1	z, z^2, x^2+y^2	
A_2	1	1	1	−1	1		R_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	$(x, y), (xz, yz)$	(R_x, R_y)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$	$h=10, \alpha=72°$	
A_1	1	1	1	1	z, z^2, x^2+y^2	
A_2	1	1	1	−1		R_z
E_1	2	$2\cos\alpha$	$2\cos 2\alpha$	0	$(x, y), (xz, yz)$	(R_x, R_y)
E_2	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_1	1	1	1	1	1	1	z, z^2, x^2+y^2	
A_2	1	1	1	1	−1	1		R_z
B_1	1	−1	1	−1	−1	1		
B_2	1	−1	1	−1	1	−1		
E_1	2	−2	−1	1	0	0	$(x, y), (xz, yz)$	(R_x, R_y)
E_2	2	2	−1	−1	0	0	(xy, x^2-y^2)	

$C_{\infty v}$	E	$2C_\phi$†	$\infty\sigma_v$	$h=\infty$	
$A_1(\Sigma^+)$	1	1	1	z, z^2, x^2+y^2	
$A_2(\Sigma^-)$	1	1	−1		R_z
$E_1(\Pi)$	2	$2\cos\phi$	0	$(x, y), (xz, yz)$	(R_x, R_y)
$E_2(\Delta)$	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	R_z
B_2	1	−1	1	−1	y, xz	R_y
B_3	1	−1	−1	1	x, yz	R_x

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	R_z
E	2	−1	0	$(x, y), (xz, yz), (xy, x^2-y^2)$	(R_x, R_y)

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	R_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	$(x, y), (xz, yz)$	(R_x, R_y)

The groups D_{nh}

D_{3h}, $\bar{6}2m$	E	σ_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		R_z
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)	(R_x, R_y)

D_{4h}, 4/*mmm*	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_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	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$	$h=20$	$\alpha=72°$
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_1	1	1	1	1	1	$x^2+y^2+z^2$	
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0	$(3z^2-r^2, x^2-y^2)$	
T_1	3	0	−1	−1	1		(R_x, R_y, R_z)
T_2	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_{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		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	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_1	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	−1	(x, y, z)	
T_2	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 2.67×10^3 kg.
1.5 1.5×10^3 Pa.
1.6 115 kPa.
1.7 $R = 0.082\,061\,5$ dm^3 atm K^{-1} mol^{-1}, $M = 31.9987$ g mol^{-1}.
1.8 P_4.
1.9 2.61 kg.
1.10 (a) 3.14 dm^3; (b) 28.2 kPa.
1.11 16.14 g mol^{-1}.
1.12 −270°C.
1.13 (a) (i) 1.0 atm, (ii) 270 atm.
(b) (i) 0.99 atm, (ii) 190 atm.
11.4 $a = 1.34 \times 10^{-1}$ kg m^5 s^{-2} mol^{-2}, $b = 4.36 \times 10^{-5}$ m^3 mol^{-1}.
1.15 (a) 1.12, repulsive; (b) 2.7 dm^3 mol^{-1}.
1.16 (a) 0.124 dm^3 mol^{-1}; (b) 0.112 dm^3 mol^{-1}.
1.17 (a) 8.7 cm^3; (b) −0.15 dm^3 mol^{-1}.
1.18 (a) $x_N = 0.63$, $x_H = 0.37$;
(b) $p_N = 2.5$ atm, $p_H = 1.5$ atm;
(c) 4.0 atm.
1.19 $b = 0.0493$ dm^3 mol^{-1}, $r = 1.94 \times 10^{-10}$ m, $a = 3.16$ dm^6 atm mol^{-2}.
1.20 (a) 1259 K; (b) 0.129 nm.
1.21 (a) $p = 2.6$ atm, $T = 881$ K;
(b) $p = 2.2$ atm, $T = 718$ K;
(c) $p = 1.4$ atm, $T = 356$ K.
1.22 $b = 1.3 \times 10^{-4}$ m^3 mol^{-1}, $Z = 0.67$.

Chapter 2

2.1 59 J.
2.2 −91 J.
2.3 (a) $\Delta U = \Delta H = 0$, $q = -w = 1.62 \times 10^3$ J;
(b) $\Delta U = \Delta H = 0$, $q = -w = 1.38 \times 10^3$ J;
(c) $\Delta U = \Delta H = 0$, $q = w = 0$.
2.4 $p_2 = 143$ kPa, $w = 0$, $q = 3.28 \times 10^3$ J, $\Delta U = 3.28 \times 10^3$ J.
2.5 (a) −19 J; (b) −52.8 J.
2.6 $\Delta H = q = -70.6$ kJ, $w = 5.60 \times 10^3$ J, $\Delta U = -65.0$ kJ.
2.7 −188 J.
2.8 (a) $\Delta H = q = 14.9 \times 10^3$ J, $w = -831$ J, $\Delta U = 14.1$ kJ.
(b) $\Delta H = 14.9$ kJ, $w = 0$, $\Delta U = q = 14.1$ kJ.
2.9 200 K.
2.10 −325 J.
2.11 8.5 Torr.
2.12 $C_{p,m} = 53$ J K^{-1} mol^{-1}, $C_{V,m} = 45$ J K^{-1} mol^{-1}.
2.13 $\Delta H = q = 2.0 \times 10^3$ J mol^{-1}, $\Delta U = 1.6 \times 10^3$ J mol^{-1}.
2.14 $q = 0$, $w = -3.5 \times 10^3$ J $= \Delta U$, $\Delta T = -24$ K, $\Delta H = -4.5 \times 10^3$ J.
2.15 $V_f = 0.0205$ m^3, $T_f = 279$ K, $w = -6.7 \times 10^2$ J.
2.16 $q = \Delta H = 24.0$ kJ, $w = -1.6$ kJ, $\Delta U = 22.4$ kJ.
2.17 −3053.6 kJ mol^{-1}.
2.18 −1152 kJ mol^{-1}.
2.19 $C = 68.3$ J K^{-1}, $\Delta T = +64.1$ K.
2.20 +84.40 kJ mol^{-1}.
2.21 +1.90 kJ mol^{-1}.
2.22 (a) $\Delta_r H^\ominus = -589.56$ kJ mol^{-1}, $\Delta_r U^\ominus = -582.13$ kJ mol^{-1}.
(b) $\Delta_f H^\ominus(\mathrm{HI}) = 26.48$ kJ mol^{-1}, $\Delta_f H^\ominus(\mathrm{H_2O}) = -241.82$ kJ mol^{-1}.
2.23 −760.3 kJ mol^{-1}.
2.24 +52.5 kJ mol^{-1}.
2.25 −566.93 kJ mol^{-1}.
2.26 (a) $\Delta_r H^\ominus(298\text{ K}) = -175$ kJ mol^{-1}, $\Delta_r U^\ominus(298\text{ K}) = -173$ kJ mol^{-1};
(b) $\Delta_r H^\ominus(348\text{ K}) = -176$ mol^{-1}.
2.27 −65.49 kJ mol^{-1}.
2.28 −1587 kJ mol^{-1}.
2.29 0.48 K atm^{-1}.
2.30 $\Delta U_m = +129$ J mol^{-1}, $q = +7.7465$ kJ mol^{-1}, $w = -7.62$ kJ mol^{-1}.
2.31 1.27×10^{-3} K^{-1}.
2.32 3.6×10^2 atm.
2.33 −41.2 J atm^{-1} mol^{-1}, q (supplied) $= 27.2 \times 10^3$ J.

Chapter 3

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

Chapter 4

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

4.5 272 K.

4.6 3.6 kg s^{-1}.

4.7 Frost will sublime, 0.40 kPa or more.

4.8 (a) 29.1 kJ mol^{-1}; (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^3.

5.2 18 cm^3.

5.3 8.2×10^3 kPa.

5.4 1.5×10^2 kPa.

5.5 270 g mol^{-1}.

5.6 178 g mol^{-1}.

5.7 −0.077°C.

5.8 $\Delta_{mix}G = -17.3$ J, $\Delta_{mix}S = 6.34 \times 10^{-2}$ J K^{-1}.

5.9 $\Delta_{mix}G = -3.43$ kJ, $\Delta_{mix}S = +11.5$ J K^{-1}, $\Delta_{mix}H = 0$.

5.10 (a) 1:1; (b) 0.7358.

5.11 N_2: 0.51 mmol kg^{-1}, O_2: 0.27 mmol kg^{-1}.

5.12 0.067 mol dm^{-3}.

5.13 11 kg.

5.14 14.0 kg mol^{-1}.

5.15 $a_A = 0.9701$, $x_A = 0.980$.

5.16 −3536 J mol^{-1}, 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_3; (b) 38.8 g $Ba(NO_3)_2$.

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) $p_{(final)} = 4.5$ 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 $x(ZrF_4) = 0.24$ appears at 855°C. The solid solution continues to form, and its ZrF_4 content increases until it reaches $x(ZrF_4) = 0.40$ 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) $\Delta_r G = 0$; (b) $K = 0.16841$; (c) $\Delta_r G^\ominus = 4.41$ kJ mol^{-1}.

7.2 (a) $K = 0.24$; (b) $\Delta_r G^\ominus = 19$ kJ mol^{-1}; (c) $K = 2.96$.

7.3 (a) $K = 1.3 \times 10^{54}$, $\Delta_r G^\ominus = 308.84$ kJ mol^{-1};
(b) $K = 3.5 \times 10^{49}$, $\Delta_r G^\ominus = -306.52$ kJ mol^{-1}.

7.4 (a) Mole fractions: A: 0.1782, B: 0.0302, C: 0.1162, 2D: 0.6742, Total: 0.9999; (b) $K_x = 9.6$; (c) $K = 9.6$; (d) $\Delta_r G^\ominus = -5.6$ kJ mol^{-1}.

7.5 $T_2 = 1.4 \times 10^3$ K.

7.6 $\Delta_r H^\ominus = 7.191$ kJ mol^{-1}, $\Delta_r S^\ominus = -21$ J K^{-1} mol^{-1}.

7.7 $\Delta G^\ominus = -41.0$ kJ mol^{-1}.

7.9 $x_{NO} = 1.6 \times 10^{-2}$.

7.10 (a) $\Delta_f H^\ominus = 39$ kJ mol^{-1}; (b) $\Delta_f H^\ominus = -39$ kJ mol^{-1}.

7.11 (a) At 427°C, $K = 9.24$, At 459°C, $K = 31.08$;
(b) $\Delta_r G^\ominus = -12.9$ kJ mol^{-1};
(c) $\Delta_r H^\ominus = +161$ kJ mol^{-1};
(d) $\Delta_r S^\ominus = +248$ J K^{-1} mol^{-1}.

7.12 $T = 397$ K.

7.13 $\Delta_f G^\ominus = -128.8$ kJ mol^{-1}.

7.14

(a)	R: $Ag_2CrO_4(s) + 2e^- \rightarrow 2Ag(s) + CrO_4^{2-}(aq)$	+0.45 V
	L: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36 V
	Overall (R − L): $Ag_2CrO_4(s) + 2Cl^-(aq) \rightarrow 2Ag(s) + CrO_4^{2-}(aq) + Cl_2(g)$	−0.91 V
(b)	R: $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+ 0.15 V
	L: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$	+ 0.77 V
	Overall (R − L): $Sn^{4+}(aq) + 2Fe^{2+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{3+}(aq)$	−0.62 V
(c)	R: $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2Fe^{3+}(aq)$	+1.23 V
	L: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34 V
	Overall (R − L): $Cu(s) + MnO_2(s) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + Mn^{2+}(aq) + 2H_2O(l)$	+0.89 V

7.15

(a)	R: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$	−0.83 V
	L: $2Na^+(aq) + 2e^- \rightarrow 2Na(s)$	−2.71 V
	and the cell is $Na(s)|Na^+(aq), OH^-(aq)|H_2(g)Pt$	+1.88 V
(b)	R: $I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54 V
	L: $2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 V
	and the cell is $Pt|H_2(g)|H^+(aq), I^-(aq)|I_2(s)|Pt$	+0.54 V
(c)	R: $2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 V
	L: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	0.083 V
	and the cell is $Pt|H_2(g)|H^+(aq), OH^-(aq)|H_2(g)|Pt$	0.083 V

7.16 (a) $E = E^\ominus - \dfrac{2RT}{F}\ln(\gamma_\pm b)$; (b) $\Delta_r G^\ominus = -89.89$ kJ mol^{-1};
(c) $E^\ominus = +0.223$ V.

7.17 (a) $K = 1.7 \times 10^{16}$; (b) $K = 8.2 \times 10^{-7}$.

7.18 (a) 1.4×10^{-20}; (b) 5.2×10^{-98}.

Chapter 8

8.1 $v = 1.3 \times 10^{-5}$ m s^{-1}.

8.2 $p = 1.89 \times 10^{-27}$ kg m s^{-1}, $v = 0.565$ m s^{-1}.

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^{-1};
(b) $E = 1.32 \times 10^{-15}$ J, E (per mole) = 7.98×10^5 kJ mol^{-1};
(c) $E = 1.99 \times 10^{-23}$ J, E (per mole) = 0.012 kJ mol^{-1}.

8.5 (a) $v = 0.499$ m s^{-1}; (b) $v = 665$ m s^{-1}; (c) $v = 9.98 \times 10^{-6}$ m s^{-1}.

8.6 $v = 158$ m s^{-1}.

8.7 (a) 3.52×10^{17} s^{-1}; (b) 3.52×10^{18} s^{-1}.

8.8 (a) 0; (b) $E_K = 6.84 \times 10^{-19}$ J; $v = 1.23 \times 10^6$ m s^{-1}.

8.9 (a) $E = 2.65 \times 10^{-19}$ J, or 160 kJ mol^{-1}; (b) $E = 3.00 \times 10^{-19}$ J, or 181 kJ mol^{-1}; (c) $E = 6.62 \times 10^{-31}$ J, or 4.0×10^{-10} kJ mol^{-1}.

8.10 (a) $\lambda = 1.23 \times 10^{-10}$ m; (b) $\lambda = 3.9 \times 10^{-11}$ m; (c) $\lambda = 3.88 \times 10^{-1}$ m.

8.12 $\Delta x = 100$ pm, speed (Δv): 5.8×10^5 m s^{-1}.

8.13 1.67×10^{-16} J.

8.14 $\hbar$.

Chapter 9

9.1 (a) 2.14×10^{-19} J, 1.34 eV, 1.08×10^4 cm^{-1}, 129 kJ mol^{-1};
(b) 3.48×10^{-19} J, 2.17 eV, 1.75×10^4 cm^{-1}, 210 kJ mol^{-1}.

9.2 (a) $P = 0.031$; (b) $P = 0.029$.

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

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

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

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 $\lambda = 13.2$ µm.

9.11 $\lambda = 18.7$ µm.

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

10.5 $\langle V \rangle = -\dfrac{Z^2 e^2}{16\pi\varepsilon_0 a_0}, \langle E_K \rangle = \dfrac{\hbar^2 Z^2}{8ma_0^2}$.

10.6 $P_{3s} = 4\pi r^2 \left(\dfrac{1}{4\pi}\right) \times \left(\dfrac{1}{243}\right) \times \left(\dfrac{Z}{\alpha_0}\right)^3 \times (6 - 6\rho + \rho^2)^2 e^{-\rho}$,
$r = 0.74\ a_0/Z$, 4.19 a_0/Z and 13.08 a_0/Z.

10.7 $r = 1.76\ a_0/Z$.

10.8 (a) angular momentum $= 6\frac{1}{2}h = 2.45 \times 10^{-34}$ J s, angular nodes = 2, radial nodes = 1;
(b) angular momentum $= 2\frac{1}{2}h = 1.49 \times 10^{-34}$ J s, angular nodes = 1, radial nodes = 0;
(c) angular momentum $= 2\frac{1}{2}h = 1.49 \times 10^{-34}$ 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 $^1F_3$; $^3F_4$; $^3F_3$; $^3F_2$; $^1D_2$; $^3D_3$; $^3D_2$; $^3D_1$; $^1P_1$; $^3P_2$; $^3P_1$; $^3P_0$, the $^3F_2$ 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) $^2D_{5/2}$ and $^2D_{3/2}$ (b) $^2P_{3/2}$ and $^2P_{1/2}$.

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) C_2 and CN; (b) NO, O_2 and F_2.

11.4 BrCl is likely to have a shorter bond length than $BrCl^-$; it has a bond order of 1, while $BrCl^-$ has a bond order of 1/2.

11.5 The sequence O_2^+, O_2, O_2^-, O_2^{2-} has progressively longer bonds.

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

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

11.8 Not appropriate.

11.9 $E_{\text{trial}} = \dfrac{-\mu e^4}{12\pi^3 \varepsilon_0^2 \hbar^2}$.

11.10 3.39×10^{-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) 19.31368β; (b) 19.44824β.

Chapter 12

12.1 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) CH_3Cl.

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 XeO_2F_2; (b) none are chiral.

12.12 NO_3^-: p_x and p_y, SO_3: all d orbitals except d_z^2.

12.13 A_2.

12.14 (a) B_{3U}(x-polarized), B_{2U}(y-polarized), B_{1U}(z-polarized); (b) A_{1U} or E_{1U}.

12.15 Yes, it is zero.

Chapter 13

13.1 (a) 7.73×10^{-32} J m^{-3} s; (b) $\nu = 6.2 \times 10^{-28}$ 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 $\nu = 3.4754 \times 10^{11}\ s^{-1}$.
13.6 (a) $I = 3.307 \times 10^{-47}$ kg m^2; (b) $R = 141$ pm.
13.7 (a) $I = 5.420 \times 10^{-46}$ kg m^2; (b) $R = 162.8$ pm.
13.8 $R = 116.21$ pm.
13.9 $R_{CO} = 116.1$ pm; $R_{CS} = 155.9$ pm.
13.10 $\tilde{\nu}_{Stokes} = 20\,603\ cm^{-1}$.
13.11 $R = 141.78$ pm.
13.12 (a) H_2O, C_{2V}; (b) H_2O_2, C_2; (c) NH_3, C_{3V}; (d) N_2O, $C_{\infty V}$.
13.13 (a) CH_2Cl_2; (b) CH_3CH_3; (d) N_2O.
13.14 $k = 0.71\ N\ m^{-1}$.
13.15 28.4 per cent.
13.16 $k = 245.9\ N\ m^{-1}$.
13.17 (a) 0.212; (b) 0.561.
13.18 DF: $\tilde{\nu} = 3002.3\ cm^{-1}$, DCl: $\tilde{\nu} = 2143.7\ cm^{-1}$, DBr: $\tilde{\nu} = 1885.8\ cm^{-1}$, DI: $\tilde{\nu} = 1640.1\ cm^{-1}$.
13.19 $\tilde{\nu} = 2374.05\ cm^{-1}$, $x_e = 6.087 \times 10^{-3}$.
13.20 $D_0 = 3.235 \times 10^4\ cm^{-1} = 4.01$ eV.
13.21 $\tilde{\nu}_R = 2347.16\ cm^{-1}$.
13.22 (a) CH_3CH_3; (b) CH_4; (c) CH_3Cl.
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 $\varepsilon = 7.9 \times 10^5\ cm^2\ mol^{-1}$.
14.4 $1.33 \times 10^{-3}\ mol\ dm^{-3}$.
14.5 $A = 1.56 \times 10^8\ dm^3\ mol^{-1}\ cm^{-2}$.
14.6 Rise.
14.7 $\varepsilon = 522\ dm^3\ mol^{-1}\ cm^{-1}$.
14.8 $\varepsilon = 128\ dm^3\ mol^{-1}\ cm^{-1}$, $T = 0.13$.
14.9 (a) 0.010 cm; (b) 0.033 cm.
14.10 (a) $1.39 \times 10^8\ dm^3\ mol^{-1}\ cm^{-2}$; (b) 1.39×10^9 m mol^{-1}.
14.11 Stronger.

Chapter 15

15.1 $\nu = 649$ MHz.
15.2 $E_{m_I} = -2.35 \times 10^{-26}$ J, 0, $+2.35 \times 10^{-26}$ J.
15.3 47.3 MHz.
15.4 (a) $\Delta E = 2.88 \times 10^{-26}$ J; (b) $\Delta E = 5.77 \times 10^{-24}$ J.
15.5 3.523 T.
15.6

	B/T	^{14}N	^{19}F	^{31}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) 4.3×10^{-7}; (b) 2.2×10^{-6}; (c) 1.34×10^{-5}.
15.8 (a) δ is independent of both B and υ. (b) $\dfrac{\nu - \nu°(800\ MHz)}{\nu - \nu°(60\ MHz)} = 13$.
15.9 (a) 4.2×10^{-6} T; (b) 3.63×10^{-5} T. Spectrum appears narrower at 650 MHz.
15.11 $2.9 \times 10^3\ s^{-1}$.
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 $B_1 = 9.40 \times 10^{-4}$ T, 6.25 µs.
15.16 1.3 T.
15.17 $g = 2.0022$.
15.18 2.2 mT, $g = 1.992$.
15.19 Eight equal parts at $\pm 1.445 \pm 1.435 \pm 1.055$ 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 $T = 623$ K.
16.2 (a) 15.9 pm, 5.04 pm; (b) 2.47×10^{26}, 7.82×10^{27}.
16.3 $\dfrac{qXe}{qHe} = 187.9$.
16.4 $q = 4.006$.
16.5 $E = 7.605\ kJ\ mol^{-1}$.
16.6 213 K.
16.7 (a) 0.997, 0.994; (b) 0.999 99, 0.999 98.
16.8 (a) (i) $\dfrac{n_2}{n_1} = 1.39 \times 10^{-11}$, $\dfrac{n_3}{n_1} = 1.93 \times 10^{-22}$;
(ii) $\dfrac{n_2}{n_1} = 0.368$, $\dfrac{n_3}{n_1} = 0.135$;
(iii) $\dfrac{n_2}{n_1} = 0.779$, $\dfrac{n_3}{n_1} = 0.607$;
(b) $q = 1.503$; (c) $U_m = 88.3\ J\ mol^{-1}$;
(d) $C_v = 3.53\ J\ K^{-1}\ mol^{-1}$; (e) $S_m = 6.92\ J\ K^{-1}\ mol^{-1}$.
16.9 7.26 K.
16.10 (a) 147 J K^{-1} mol^{-1}; (b) 169.6 J K^{-1} mol^{-1}.
16.11 10.7 J K^{-1} mol^{-1}.
16.12 (a)

Chapter 17

17.1 (a) $O_3 : 3R$ [experimental $= 3.7R$]
(b) $C_2H_6 : 4R$ [experimental $= 6.3R$]
(c) $CO_2 : \frac{5}{2}R$ [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 $q^K = 5837$, $\theta_R = 0.8479$ K, $T = 0.3335$ K.
17.6 $S_m^R = 84.57\ J\ K^{-1}\ mol^{-1}$.
17.7 (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°C, $q^R = 7.97 \times 10^3$; (b) At 100°C, $q^R = 1.12 \times 10^4$.
17.9 (a) At 298 K, $S_m = 5.88\ J\ mol^{-1}\ K^{-1}$.
(b) At 500 K, $S_m = 16.48\ J\ mol^{-1}\ K^{-1}$.
17.10 $G_m^R - G_m^R(0) = -20.1\ kJ\ mol^{-1}$, $G_m^V - G_m^V(0) = -0.110\ kJ\ mol^{-1}$.
17.11 $-3.65\ kJ\ mol^{-1}$.
17.12 $S_m = 14.9\ J\ mol^{-1}\ K^{-1}$.
17.14 $K \approx 0.25$.

Chapter 18

18.1 SF_4.
18.2 $\mu = 1.4$ D.
18.3 $\mu = 9.45 \times 10^{-29}$ C m, $\theta = 194.0°$.
18.4 $\mu = 3.23 \times 10^{-30}$ C m, $\alpha = 2.55 \times 10^{-39}$ C^2 m^2 J^{-1}.
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^2 m^2 J^{-1}.
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^{-1}.
18.12 $p_{in} - p_{out} = 2.04 \times 10^5$ Pa.

Chapter 19

19.1 $\bar{M}_n = 68$ kg mol^{-1}, $\bar{M}_w = 69$ kg mol^{-1}.
19.2 $R_g = 1.06 \times 10^4$.
19.3 (a) $\bar{M}_n = 8.8$ kg mol^{-1}; (b) $\bar{M}_w = 11$ kg mol^{-1}.
19.4 $\tau = 9.4 \times 10^{-8}$ s.
19.5 71.
19.6 $\bar{M}_n = 120$ kg mol^{-1}.
19.7 $s = 1.47 \times 10^{-4}$ m s^{-1}.
19.8 $\bar{M} = 56$ kg mol^{-1}.
19.9 $\bar{M}_w = 3.1 \times 10^3$ kg mol^{-1}.
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	$\boxed{38.2}$
200	0.378	22.2	$\boxed{44.4}$
220	0.535	32.3	$\boxed{64.6}$

20.6 $D = 0.054$ cm.
20.7 $V = 1.2582$ nm^3.
20.8 $d = 5$, $d = 2.90$ g cm^{-3}.
20.9 $d_{322} = 182$ pm.
20.10 (100), (110), (111), and (200).
20.11

hkl	d_{hkl}/pm	θ_{hkl}/°
100	574.1	$\boxed{4.166}$
010	796.8	$\boxed{3.000}$
111	339.5	$\boxed{7.057}$

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 $\frac{2V_{atom}}{V_{cell}} = 0.370$.
20.18 contraction.
20.20 $\lambda = 252$ pm.
20.21 $\Delta_L H^{\ominus}(MgBr_2, s) = 2421$ kJ mol^{-1}.
20.23 strain $= 5.8 \times 10^{-2}$.
20.24 $\Delta V = 0.003$ dm^3.
20.25 p-type.
20.26 2.71×10^4 H.
20.27 5.
20.28 -8.2×10^{-4} cm^3 mol^{-1}.
20.29 $\chi_m = 1.58 \times 10^{-8}$ m^3 mol^{-1}, dimerization occurs.
20.30 2.52 = effective unpaired spins, theoretical number = 2.
20.31 $\chi_m = 1.85 \times 10^{-7}$ m^3 mol^{-1}.
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^{-1}; (b) $\lambda = 4 \times 10^4$ m; (c) $z = 0.01$ s^{-1}.
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^{-1}.
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 $M_{fluorocarbon} = 554$ g mol^{-1}.
21.11 $t = 1.5 \times 10^4$ s.
21.12 0.17 J m^{-2} s^{-1}.
21.13 1.61×10^{-19} m^2.
21.14 22 J s^{-1}.
21.15 3.00×10^{-19} m^2.
21.16 1.00×10^5 Pa.
21.17 (a) At 273 K: $\eta = 0.95 \times 10^{-5}$ kg m^{-1} s^{-1};
(b) At 298 K: $\eta = 0.99 \times 10^{-5}$ kg m^{-1} s^{-1};
(c) At 1000 K: $\eta = 1.81 \times 10^{-5}$ kg m^{-1} s^{-1}.
21.18 (a) $\kappa = 0.0114$ J m^{-1} s^{-1} K^{-1}, 0.017 J s^{-1};
(b) $\kappa = 9.0 \times 10^{-3}$ J m^{-1} s^{-1} K^{-1}, 0.014 J s^{-1}.
21.19 52.0×10^{-7} kg m^{-1} s^{-1}, $d = 923$ pm.
21.20 $\kappa = 9.0 \times 10^{-3}$ J m^{-1} s^{-1} K^{-1}.
21.21 (a) $D = 0.107$ m^2 s^{-1}, $J = 0.87$ mol m^{-2} s^{-1};
(b) $D = 1.07 \times 10^{-5}$ m^2 s^{-1}, $J = 8.7 \times 10^{-5}$ mol m^{-2} s^{-1};
(c) $D = 7.13 \times 10^{-8}$ m^2 s^{-1}, $J = 5.8 \times 10^{-7}$ mol m^{-2} s^{-1}.
21.22 4.09×10^{-3} S m^2 mol^{-1}.
21.23 4.81×10^{-5} m V^{-1} s^{-1}.
21.24 0.604.
21.25 $\Lambda_m^{\circ}(MgI_2) = 25.96$ mS m^2 mol^{-1}.
21.26 F^-: $u = 5.74 \times 10^{-8}$ m^2 V^{-1} s^{-1};
Cl^-: $u = 7.913 \times 10^{-8}$ m^2 V^{-1} s^{-1};
Br^-: $u = 8.09 \times 10^{-8}$ m^2 V^{-1} s^{-1}.
21.27 1.09×10^{-9} m^2 s^{-1}.
21.28 4.1×10^3 s.

21.29 207 pm.
21.30 200×10^{-11} s = 20 ps.
21.31 Iodine: (a) 78 s; (b) 7.8×10^3 s.
Sucrose: (a) 3.2×10^2 s; (b) 3.2×10^4 s.

Chapter 22

22.1 Rates of consumption of A = 1.0 mol dm^{-3} s^{-1}; B = 3.0 mol dm^{-3} s^{-1}; C = 1.0 mol dm^{-3} s^{-1}; D = 2.0 mol dm^{-3} s^{-1}.
22.2 Rate of consumption of B = 1.00 mol dm^{-3} s^{-1}.
Rate of reaction = 0.33 mol dm^{-3} s^{-1}.
Rate of formation of C = 0.33 mol dm^{-3} s^{-1}.
Rate of formation of D = 0.66 mol dm^{-3} s^{-1}.
Rate of consumption of A = 0.33 mol dm^{-3} s^{-1}.
22.3 K: dm^3 mol^{-2} s^{-1}. (a) $v = \dfrac{d[A]}{dt} = -k[A][B]^2$; (b) $v = \dfrac{d[C]}{dt} = k[A][B]^2$.
22.4 $v = k[A][B][C]^{-1}$, K: s^{-1}.
22.5 2.00.
22.6 Reaction order = 0.
22.7 $t_{1/2} = 1.80 \times 10^6$ s, (a) $p = 31.5$ kPa; (b) $p = 29.0$ kPa.
22.8 (a) $k = 3.47 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}; (b) $t_{1/2}(A) = 2.4$ h; $t_{1/2}(B) = 0.44$ h.
22.9 (a) Second-order units: m^3 molecule^{-1} s^{-1}, Third-order units: m^6 molecule^{-2} s^{-1}; (b) Second-order units; Pa^{-1} s^{-1}, Third-order units; Pa^{-2} s^{-1}.
22.10 (a) 6.5×10^{-3} mol dm^{-3}; (b) 0.025 mol dm^{-3}.
22.11 1.5×10^6 s.
22.12 $t_{1/3} = \dfrac{3^{n-1} - 1}{k(n-1)}[A]_0^{1-n}$.
22.13 $K_f = 1.7 \times 10^{-7}$ s^{-1}, $k_r = 8.3 \times 10^8$ dm mol^{-1} s^{-1}.
22.14 $E_a = 9.9$ kJ mol^{-1}, $A = 0.94$ dm^3 mol^{-1} s^{-1}.
22.15 (a) $k_T/k_H \approx 0.06$; (b) $k_{18}/k_{16} \approx 0.89$.
22.16 $k_a = 9.9 \times 10^{-6}$ s^{-1} Pa^{-1} = 9.9 s^{-1} MPa^{-1}.

Chapter 23

23.2 $\dfrac{d[R_2]}{dt} = -k_1[R_2] - k_2\left(\dfrac{k_1}{k_4}\right)^{1/2}[R_2]^{3/2}$.
23.3 (a) Does not occur. (b) $p = 1.3 \times 10^2$ Pa to 3×10^4 Pa.
23.4 $\dfrac{k_1 k_2 K_a^{1/2}}{k_1'}[HA]^{3/2}[B]$.
23.5 $\dfrac{d[A_2]}{dt} = -k_1[A_2]$.
23.6 $v_{max} = 2.57 \times 10^{-4}$ mol dm^{-3} s^{-1}.
23.7 1.5×10^{-5} moles of photons.
23.8 $\Phi = 1.11$.

Chapter 24

24.1 $z = 6.64 \times 10^9$ s^{-1}, $Z_{AA} = 8.07 \times 10^{34}$ m^{-3} s^{-1}, 1.6 per cent.
24.2 (a) (i) 2.4×10^{-3}, (ii) 0.10; (b) (i) 7.7×10^{-27}, (ii) 1.6×10^{-10}.
24.3 (a) (i) 1.2, (ii) 1.03; (b) (i) 7.4, (ii) 1.3.
24.4 $k = 1.7 \times 10^{-12}$ dm^{-3} mol^{-1} s^{-1}.
24.5 $k_d = 3.2 \times 10^7$ m^3 mol^{-1} s^{-1} or 3.2×10^{10} dm^3 mol^{-1} s^{-1}.
24.6 (a) $k_d = 1.97 \times 10^6$ m^3 mol^{-1} s^{-1}; (b) $k_d = 2.4 \times 10^5$ m^3 mol^{-1} s^{-1}.
24.7 $k_d = 1.10 \times 10^7$ m^3 mol^{-1} s^{-1} or 1.10×10^{10} dm^3 mol^{-1} s^{-1}, $t_{1/2} = 5.05 \times 10^{-8}$ s.
24.8 $P = 1.41 \times 10^{-3}$.
24.9 $v = 1.54 \times 10^8$ mol dm^{-3} s^{-1}.
24.10 $\Delta^{\ddagger}H = 48.52$ kJ mol^{-1}, $\Delta^{\ddagger}S = -32.2$ J K^{-1} mol^{-1}.
24.11 $\Delta^{\ddagger}G = 46.8$ kJ mol^{-1}.
24.12 $\Delta^{\ddagger}S = -93$ J K^{-1} mol^{-1}.
24.13 $\Delta^{\ddagger}S = -80.0$ J K^{-1} mol^{-1}.
24.14 (a) $\Delta^{\ddagger}S = -24.1$ J K^{-1} mol^{-1}; (b) $\Delta^{\ddagger}H = 27.5$ kJ mol^{-1}; (c) $\Delta^{\ddagger}G = 34.7$ kJ mol^{-1}.
24.15 $k_2^{\circ} = 1.08$ dm^6 mol^{-2} min^{-1}.
24.16 $\lambda = 1.531$ eV, $\langle H_{DA}\rangle = 9.39 \times 10^{-24}$ J.
24.17 $k_{et} = 1.4 \times 10^3$ s^{-1}.

Chapter 25

25.1 (a) (i) 2.88×10^{19} cm^{-2} s^{-1}, (ii) 5.75×10^{13} cm^{-2} s^{-1}; (b) (i) 3.81×10^{19} cm^{-2} s^{-1}, (ii) 7.60×10^{13} cm^{-2} s^{-1}.
25.2 $p = 7.3 \times 10^2$ Pa.
25.3 6.6×10^4 s^{-1}.
25.4 $A = 18.8$ m^2.
25.5 $V_{mon} = 9.7$ cm^3.
25.6 $t_{1/2} = 200$ s.
25.7 $E_d = 3.7 \times 10^3$ 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: 4.9×10^{-11} s, At 800 K: 2.4×10^{-12} s; (b) At 400 K: 1.6×10^{13} s, At 800 K: 1.4 s.
25.11 $p_2 = 6.50$ kPa.
25.12 (a) $\theta = \dfrac{Kp}{1+Kp}$; (b) $\theta = \dfrac{(Kp)^{1/2}}{1+(Kp)^{1/2}}$; (c) $\theta = \dfrac{(Kp)^{1/3}}{1+(Kp)^{1/3}}$. A plot of θ 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 $\Delta_{ad}H^{\ominus} = -6.40$ kJ mol^{-1}.
25.14 $E_d = 2.85 \times 10^5$ J mol^{-1}. (a) $t = 1.48 \times 10^{36}$ s; (b) $t = 1.38 \times 10^{-4}$ s.
25.15 $\varepsilon = 2.8 \times 10^8$ Vm^{-1}.
25.16 167 mV.
25.17 $j_0 = 1.6$ mA cm^{-2}.
25.18 $j_2 = 8.5$ mA cm^{-2}.
25.19 (a) $j = 0.34$ A cm^{-2};
(b) $j = 0.34$ A cm^{-2}. The validity of the Tafel equation improves as the overpotential increases.
25.20 $j_{lim} = 1.3$ A m^{-2}.
25.21 $[Fe^{2+}] = 4 \times 10^{-6}$ 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 $r = 0.1$: $j/j_0 = 1.5$ A cm^{-2},
At $r = 1$: $j/j_0 = 4.8$ A cm^{-2},
At $r = 10$: $j/j_0 = 15$ A cm^{-2}.
25.24 0.61 V.
25.25 For the Cu, $H_2|H^+$ electrode: $N = 6.2 \times 10^{12}$ s^{-1} cm^{-2}, $f = 4.2 \times 10^{-3}$ s^{-1}.
For the Pt|Ce^{4+}, Ce^{3+} electrode: $N = 2.5 \times 10^{14}$ s^{-1} cm^{-2}, $f = 0.17$ 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 $E^{\ominus} = 1.80$ V, $P = 0.180$ W.
25.32 3.0 mm y^{-1}.

Solutions to odd problems

Chapter 1

1.1 $-233°N$.

1.3 $-272.95°C$.

1.5 (a) $\Delta p = 0.0245$ kPa; (b) $p = 9.14$ kPa; (c) $\Delta p = 0.0245$ kPa.

1.7 (a) $V_m = 12.5\ dm^3\ mol^{-1}$; (b) $V_m = 12.3\ dm^3\ mol^{-1}$.

1.9 (a) $0.944\ dm^3\ mol^{-1}$;
(b) $2.69\ dm^3\ mol^{-1}$, $2.67\ dm^3\ mol^{-1}$;
(c) $5.11\ dm^3\ mol^{-1}$

1.11 (a) $0.1353\ dm^3\ mol^{-1}$; (b) 0.6957; (c) 0.72.

1.13 $b = 59.4\ cm^3\ mol^{-1}$, $a = 5.649\ dm^6\ atm\ mol^{-2}$, $p = 21$ atm.

1.15 $B = b - \dfrac{a}{RT}$, $C = b^2$, $b = 34.6\ cm^3\ mol^{-1}$, $a = 1.26\ dm^6\ atm\ mol^{-2}$.

1.17 $V_c = \dfrac{3C}{B}$, $T_c = \dfrac{B^2}{3RC}$, $p_c = \dfrac{B^3}{27C^2}$, $Z_c = \dfrac{1}{3}$

1.19 $B' = 0.082\ atm^{-1}$, $B = 2.0\ dm^3\ mol^{-1}$.

1.21 No.

1.23 0.011.

1.25 $4.1 \times 10^8\ dm^3$

1.27 (a) 0.00; (b) -0.72

1.31 $h = 51.5$ km.
$p = 3.0 \times 10^{-3}$ bar.

Chapter 2

2.1 $T_1 = 273\ K = T_3$, $T_2 = 546$ K
Step $1 \to 2$: $w = -2.27 \times 10^3$ J
$\Delta U = +3.40 \times 10^3$ J
$q = +5.67 \times 10^3$ J
$\Delta H = +5.67 \times 10^3$ J
Step $2 \to 3$: $w = 0$
$q_v = \Delta U = -3.40 \times 10^3$ J
$\Delta H = -5.67 \times 10^3$ J
Step $3 \to 1$: $\Delta U = \Delta H = 0$
$-q = w = +1.57 \times 10^3$ J
Cycle: $\Delta U = \Delta H = 0$
$q = -w = +0.70 \times 10^3$ J

2.3 $w = 0$, $\Delta U = +2.35$ kJ, $\Delta H = +3.03$ kJ,

2.5 (a) $w = 0$, $\Delta U = +6.19$ kJ, $q = +6.19$ kJ, $\Delta H = +8.67$ kJ;
(b) $q = 0$, $\Delta U = -6.19$ kJ, $\Delta H = -8.67$ kJ, $w = -6.19$ kJ;
(c) $\Delta U = \Delta H = 0$, $-q = w = +4.29$ kJ.
(a) $w_0 = -1.7$ kJ; (b) $w = -1.8$ kJ; (c) $w = -1.5$ kJ.

2.7 $-87.33\ kJ\ mol^{-1}$.

2.9 $\Delta_r H^{\ominus} = +17.7\ kJ\ mol^{-1}$, $\Delta_f H^{\ominus}$(metallocene, 583 K) $= +116.0\ kJ\ mol^{-1}$.

2.11 (c) $n = 0.903$, $k = -73.7\ kJ\ mol^{-1}$.

2.13 $\Delta_c H^{\ominus} = 25\,968\ kJ\ mol^{-1}$, $\Delta_f H^{\ominus}(C_{60}) = 2357\ kJ\ mol^{-1}$.

2.15 (a) $240\ kJ\ mol^{-1}$; (b) $228\ kJ\ mol^{-1}$.

2.17 $41.40\ J\ K^{-1}\ mol^{-1}$.

2.19 3.60 kJ.

2.21 (a) $dz = (2x - 2y + 2)dx + (4y - 2x - 4)dy$

(c) $dz = \left(y + \dfrac{1}{x}\right)dx + (x - 1)dy$

2.25 (a) $\left(\dfrac{\partial H}{\partial U}\right)_p = 1 + p\left(\dfrac{\partial V}{\partial U}\right)_p = 1 + \dfrac{p}{(\partial U/\partial V)_p}$

(b) $\left(\dfrac{\partial H}{\partial U}\right)_p = 1 + \dfrac{p}{(\partial U/\partial V)_p} = 1 + p\left(\dfrac{\partial V}{\partial U}\right)_p$

2.27 (a) -1.5 kJ, (b) -1.6 kJ.

2.29 increase.

2.37 (a) $\mu = \dfrac{aT^2}{C_p}$

(b) $C_v = C_p - R\left(1 + \dfrac{2apT}{R}\right)^2$

2.39 7.4%.

2.41 (a) -25 kJ; (b) 9.7 m; (c) 39 kJ; (d) 15 m.

2.45 $\Delta T = 2°C$, $\Delta h = 1.6$ m, $\Delta T = 1°C$, $\Delta h = 0.8$ m, $\Delta T = 3.5°C$, $\Delta h = 2.8$ m.

2.47 (a) $23.5\ K\ MPa^{-1}$; (b) $14.0\ K\ MPa^{-1}$.

Chapter 3

3.1 (a) $\Delta_{trs}S(l \to s, -5°C) = -21.3\ J\ K^{-1}\ mol^{-1}$, $\Delta S_{sur} = +21.7\ J\ K^{-1}\ mol^{-1}$, $\Delta S_{total} = +0.4\ J\ K^{-1}\ mol^{-1}$.
(b) $\Delta_{trs}S\ (l \to g, T) = +109.7\ J\ K^{-1}\ mol^{-1}$, $\Delta S_{sur} = -111.2\ J\ K^{-1}\ mol^{-1}$, $\Delta S_{total} = -1.5\ J\ K^{-1}\ mol^{-1}$.

3.3 (a) $q(Cu) = 43.9$ kJ, $q(H_2O) = -43.9$ kJ, $\Delta S(H_2O) = -118.1\ J\ K^{-1}$, $\Delta S(Cu) = 145.9\ J\ K^{-1}$, $\Delta S(\text{total}) = 28\ J\ K^{-1}$.
(b) $\theta = 49.9°C = 323.1$ K, $q(Cu) = 38.4\ kJ = -q(H_2O)$, $\Delta S(H_2O) = -119.8\ J\ K^{-1}$, $\Delta S(Cu) = 129.2\ J\ K^{-1}$, $\Delta S(\text{total}) = 9\ J\ K^{-1}$.

3.5

	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
ΔU	0	−3.74 kJ	0	+3.74 kJ	0
ΔH	0	−6.23 kJ	0	+6.23 kJ	0
ΔS	$+19.1\ J\ K^{-1}$	0	$-19.1\ J\ K^{-1}$	0	0
ΔS_{tot}	0	0	0	0	0
ΔG	−11.5 kJ	Indeterminate	+11.5 kJ	Indeterminate	0

3.7 (a) $200.7\ J\ K^{-1}\ mol^{-1}$; (b) $232.0\ J\ K^{-1}\ mol^{-1}$.

3.9 $\Delta S = nC_{p,m} \ln\dfrac{T_f}{T_h} + nC_{p,m} \ln\dfrac{T_f}{T_c}$, $\Delta S = +22.6\ J\ K^{-1}$.

3.11 (a) $63.88\ J\ K^{-1}\ mol^{-1}$; (b) $66.08\ J\ K^{-1}\ mol^{-1}$.

3.13 $H_m^{\ominus}(200\ K) - H_m^{\ominus}(0) = 32.1\ kJ\ mol^{-1}$.

3.15 $46.60\ J\ K^{-1}\ mol^{-1}$.

3.17 (a) $-7\ kJ\ mol^{-1}$; (b) $+107\ kJ\ mol^{-1}$.

3.29 $\pi_T \approx \dfrac{p^2}{R} \times \dfrac{\Delta B}{\Delta T}$

(a) 3.0×10^{-3} atm; (b) 0.30 atm.

3.31 $\pi_T = \dfrac{nap}{RTV}$

3.33 $T\,dS = C_p dT - \alpha TV\,dp$, $q_{rev} = -\alpha TV\,\Delta p$, $q_{rev} = -0.50$ kJ

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

$f = 0.9991$ atm

3.37 $-21\ \mathrm{kJ\ mol^{-1}}$.

3.39 13 per cent increase.

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

$\varepsilon = 0.47$

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

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

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

Chapter 4

4.1 196.0 K, 11.1 Torr.

4.3 (a) $5.56\ \mathrm{kPa\ K^{-1}}$; (b) 2.5 per cent.

4.5 (a) $-1.63\ \mathrm{cm^3\ mol^{-1}}$; (b) $+30.1\ \mathrm{dm^3\ mol^{-1}}$, $+0.6\ \mathrm{kJ\ mol^{-1}}$.

4.7 22°C.

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

4.11 (b) 171.18 K; (c) $T = 383.6$ K; (d) $33.0\ \mathrm{kJ\ mol^{-1}}$.

4.15 9.8 Torr.

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

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

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

Chapter 5

5.1 $k_A = 15.58$ kPa, $k_B = 47.03$ kPa.

5.3 $V_{salt} = -1.4\ \mathrm{cm^3\ mol^{-1}}$, $V_{H_2O} = 18.04\ \mathrm{cm^3\ mol^{-1}}$.

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

5.7 4 ions.

5.11 (a) propionic acid: $V_1 = V_{m,1} + a_0x_2^2 + a_1(3x_1 - x_2)x_2^2$,

oxane: $V_2 = V_{m,2} + a_0x_1^2 + a_1(x_1 - 3x_2)x_1^2$,

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

5.13 $K_H = 371$ bar, $\gamma_{CO_2} = 1.01$ (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 $\Delta_{mix}G = -4.6$ kJ.

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

5.19 $80.36\ \mathrm{cm^3\ mol^{-1}}$.

5.25 p_{N_2} at 4.0 atm = 56 µg, p_{N_2} at 1.0 atm = 14 µg, increase = 1.7×10^2 µg N_2.

5.29 (a) $\mathrm{g\ cm\ K^{-1}\ mol^{-1}}$,

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

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

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

Chapter 6

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

6.3 Temperature (γ_{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 $MgCu_2$: 16 per cent mg by mass, Mg_2Cu: 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_2Si = 1314°C; CaSi = 1324°C. Incongruent melting compounds: $CaSi_2$ = 1040°C;

(b) At 1000°C, the phases at equilibrium will be Ca(s) and liquid (13 at per cent Si). Relative amounts, $n_{Ca}/n_{liq} = 2.86$;

(c) (i) $n_{Si}/n_{liq} = 0.53$ at slightly above 1030°C, (ii) $n_{Si}/n_{CaSi_2} = 0.665$ 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) $y(\mathrm{MgO}) = 0.18$, $x(\mathrm{MgO}) = 0.35$, (c) $c = 2640$°C.

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

Chapter 7

7.1 (a) $\Delta_r G^{\ominus} = +4.48\ \mathrm{kJ\ mol^{-1}}$; (b) $p_{IBr} = 0.101$ atm.

7.3 $\Delta_f H^{\ominus} = 8.48\ R$.

7.5 $\Delta_r G^{\ominus}(T)/(\mathrm{kJ\ mol^{-1}}) = 78 - 0.161 \times (T/\mathrm{K})$.

7.7 First experiment, $K = 0.740$, second experiment, $K = 5.71$, enthalpy of dimerization = $-103\ \mathrm{kJ\ mol^{-1}}$.

7.9 $\Delta H^{\ominus} = +158\ \mathrm{kJ\ mol^{-1}}$.

7.11 (a) At 298 K: 1.2×10^8; (b) At 700 K: 2.7×10^3.

7.13 (a) $CuSO_4$: 4.0×10^{-3}; $ZnSO_4$: 1.2×10^{-2}; (b) $\gamma_\pm(CuSO_4) = 0.74$, $\gamma_\pm(ZnSO_4) = 0.60$; (c) $Q = 5.9$; (d) $E^{\ominus} = +1.102$ V; (e) $E = +1.079$ V.

7.15 pH = 2.0.

7.17 $E^{\ominus} = +0.268\ 43$ V, $\gamma_\pm = 0.9659$ (1.6077 mmol kg^{-1}), 0.9509 (3.0769 mmol kg^{-1}), 0.9367 (5.0403 mmol kg^{-1}), 0.9232 (7.6938 mmol kg^{-1}), 0.9094 (10.9474 mmol kg^{-1}),

7.19 $\gamma = 0.533$.

7.21 (a) $\left(\dfrac{\partial E}{\partial p}\right)_{T,n} = -\dfrac{\Delta_r V}{\nu F}$;

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

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

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

7.23 -1.15 V.

7.25 $\xi = 1 - \left(\dfrac{1}{1 + ap/p^{\ominus}}\right)^{1/2}$

7.31 Yes.

7.33 (b) +0.206 V.

7.35 (iv) $HNO_3{\cdot}3H_2O$ is most stable.

Chapter 8

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

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

8.5 (a) 9.0×10^{-6}; (b) 1.2×10^{-6}.

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

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 $\dfrac{\mathrm{d}^2}{\mathrm{d}x^2}$; (b,d) are eigenfunctions of $\dfrac{\mathrm{d}^2}{\mathrm{d}x^2}$, but not of $\dfrac{\mathrm{d}}{\mathrm{d}x}$.

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

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

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

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

Chapter 9

9.1 $E_2-E_1=1.24\times10^{-39}$ J, $n=2.2\times10^{9}$ J, $E_n-E_{n-1}=1.8\times10^{-30}$ J.

9.3 $E_1=1.30\times10^{-22}$ J, minimum angular momentum $=\pm\eta$.

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

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

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

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

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

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

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

9.25 $\theta=\arccos\dfrac{m_l}{\{l(l+1)\}^{1/2}}$, 54°44′.

9.31 (a) $\Delta E=3.3\times10^{-19}$ J; (b) $v=4.95\times10^{-14}$ J s^{-1}; (c) lower, increases.

9.33 $\omega=2.68\times10^{-14}$ J s^{-1}.

9.35 (a) $l_z=5.275\times10^{-34}$ J s, $E_{\pm5}=1.39\times10^{-24}$ J; (b) $v=9.2\times10^{8}$ Hz.

9.37 $F=5.8\times10^{-11}$ N.

Chapter 10

10.1 $n_2\to6$, transitions occur at 12 372 nm, 7503 nm, 5908 nm, 5129 nm, . . . , 3908 nm (at $n_2=15$), converging to 3282 nm as $n_2\to\infty$.

10.3 $R_{Li^{2+}}=987\,663$ cm^{-1}, the Balmer transitions lie at $\tilde{\nu}=137\,175$ cm^{-1}, 85 187 cm^{-1}, 122.5 eV.

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

10.7 3.3429×10^{-24} kg, $\dfrac{I_D}{I_H}=1.000\,272$.

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

10.11 ±106 pm.

10.13 (b) For 3*s*, $\rho_{\text{node}}=3+\sqrt{3}$ and $\rho_{\text{node}}=3-\sqrt{3}$, no nodal plane; for 3_{px}, $\rho_{\text{node}}=0$ and $\rho_{\text{node}}=4$, *yz* nodal plane ($\phi=90°$); for $3d_{xy}$, $\rho_{\text{node}}=0$, *xz* nodal plane ($\phi=0$) and *yz* nodal plane ($\phi=90°$); (c) $(r)_{3s}=\dfrac{27a_0}{2}$.

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

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

10.27 (a) receeding; $s=3.381\times10^{5}$ ms^{-1}.

Chapter 11

11.3 $R=2.1a_0$.

11.7 (a) $P=8.6\times10^{-7}$ / $P=2.0\times10^{-6}$;
(b) $P=8.6\times10^{-7}$ / $P=2.0\times10^{-6}$;
(c) $P=3.7\times10^{-7}$ / $P=0$;
(d) $P=4.9\times10^{-7}$/ $P=5.5\times10^{-7}$.

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) C_2H_4: −3.813, C_4H_6: −4.623, C_6H_8: −5.538, C_8H_{10}: −5.873; (b) 8.913 eV.

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

Chapter 12

12.1 (a) D_{3d}; (b) chair: D_{3d}, boat: C_{2V}; (c) D_{2h}; (d) D_3; (d) D_{4d}; (i) Polar: Boat C_6H_{12}; (ii) Chiral: $[Co(en)_3]^{3+}$.

12.3 $C_2\sigma_h=i$.

12.7

	1	σ_x	σ_y	σ_z
1	1	σ_x	σ_y	σ_z
σ_x	σ_x	1	$i\sigma_x$	$-i\sigma_y$
σ_y	σ_y	$-i\sigma_z$	1	$i\sigma_x$
σ_z	σ_z	$i\sigma_y$	$-i\sigma_z$	1

The matrices do not form a group since the products $i\sigma_z$, $i\sigma_y$, $i\sigma_x$ 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: C_{2h}; (ii) Eclipsed: C_{2V}.

12.13 (a) C_{2V}, $f\to2A_1+A_2+2B_1+2B_2$;
(b) C_{3V}, $f\to+A_2+3E$;
(c) T_d, $f\to A_1+T_1+T_2$;
(d) O_h, $f\to A_{2U}+T_{1U}+T_{2U}$.
Lanthanide ion (a) tetrahedral complex: $f\to A_1+T_1+T_2$ in T_d symmetry, and there is one nondegenerate orbital and two sets of triply degenerate orbitals. (b) octahedral complex: $f\to A_{2U}+T_{1U}+T_{2U}$, and the pattern of splitting is the same.

12.15 irreducible representations: $4A_1+2B_1+3B_2+A_2$

Chapter 13

13.1

T/K	E/J m^{-3}	E_{class}/J m^{-3}
(a) 1500	2.136×10^{-6}	2.206
(b) 2500	9.884×10^{-4}	3.676
(c) 5800	3.151×10^{-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 $I=2.728\times10^{-47}$ kg m^2, $R=129.5$ pm, hence we expect lines at 10.56, 21.11, 31.67, . . . cm^{-1}.

13.9 218 pm.

13.11 $B=14.35$ m^{-1}, $J_{max}=26$ 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) $\tilde{\nu}=152$ m^{-1}, $k=2.72\times10^{-4}$ kg s^{-2}, $I=2.93\times10^{-46}$ kg m^2, $B=95.5$ m^{-1}.
(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 $HgCl_2$: 230, $HgBr_2$: 240, HgI_2: 250 pm.

13.27 (a) infrared active; (b) 796 cm^{-1}; (c) O_2: 2, O_2^-: 1.5, O_2^{2-}: 1; (d) $Fe_2^{3+}O_2^{2-}$; (e) Structures 6 and 7 are consistent with this observation, but structures 4 and 5 are not.

13.29 $s=0.0768$ c, $T=8.34\times10^5$ K.

13.31 $B=2.031$ cm^{-1}; $T=2.35$ K.

Chapter 14

14.1 49 364 cm^{-1}.

14.3 14 874 cm^{-1}.

14.5 $\mathcal{A}=1.1\times10^6$ dm^3 mol^{-1} cm^{-2}, Excitations from A_1 to A_1, B_1, and B_2 terms are allowed.

14.7 5.06 eV.

14.9

Hydrocarbon	E_{HOMO}/eV*
Benzene	−9.7506
Biphenyl	−8.9169
Naphthalene	−8.8352
Phenanthrene	−8.7397
Pyrene	−8.2489
Anthracene	−8.2477

14.11 (a) $\frac{n}{V}=1.7\times10^{-9}$ mol dm^{-3}, (b) $N=6.0\times10^2$.

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 4.4×10^3.

14.25 $\mathcal{A}=1.24\times10^5$ dm^3 mol^{-1} dm^{-2}.

14.27 (a) $\mathcal{A}=2.24\times10^5$ dm^3 mol^{-1} cm^{-2}; (b) A = 0.185;
(c) $\varepsilon=135$ dm^3 mol^{-1} cm^{-1}.

14.29 $V_1-V_0=3.1938$ eV, $\tilde{\nu}_1-\tilde{\nu}_0=79.538$ cm^{-1}, $\tilde{\nu}_0=2034.3$ cm^{-1}, $T_{eff}=1321$ K.

Chapter 15

15.1 $B_0=10.3$ T, $\frac{\delta N}{N}\approx2.42\times10^{-5}$, β state lies lower.

15.3 300×10^{-6} Hz ± 10 Hz, 0.29 s.

15.5 Both fit the data equally well.

15.9 Width of the CH_3 spectrum is $3a_H=6.9$ mT. The width of the CD_3 spectrum is $6a_D$. The overall width is $6a_D=2.1$ mT.

15.11 $P(N2s)=0.10$, $P(N2p_z)=0.38$, total probability: $P(N)=0.48$, $P(O)=0.52$, hybridization ratio = 3.8, $\Phi=131°$.

15.13 $\sigma_d=\frac{e^2\mu_0 Z}{12\pi m_e a_0}=1.78\times10^{-5}\,Z$.

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

Chapter 16

16.1 $W=2\times10^{40}$, $S=1.282\times10^{-21}$ J K^{-1}, $S_1=0.637\times10^{-21}$ J K^{-1}, $S_2=0.645\times10^{-21}$ J K^{-1}.

16.3 $\frac{\Delta W}{W}\approx2.4\times10^{25}$.

16.5 $T=3.5\times10^{-15}$ 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; $p_2=6.5\times10^{-11}$ at 298 K, $p_2=0.12$ at 5000 K.
(c) (i) $S_m=13.38$ J K^{-1} mol^{-1}, (ii) $S_m=18.07$ J K^{-1} mol^{-1}.

16.9 (a) $p_0=0.64$, $p_1=0.36$; (b) 0.52 kJ mol^{-1}. At 300 K, $S_m=11.2$ J K^{-1} mol^{-1}, At 500 K, $S_m=11.4$ J K^{-1} mol^{-1}.

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^{-1}, $S_m=1.63$ J K^{-1} mol^{-1}.
(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^{-1}, $S_m=8.17$ J K^{-1} mol^{-1}.

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^{-1} mol^{-1}, $S_m=15$ J K^{-1} mol^{-1}.

17.5 $q=19.90$.

17.7 $S_m^{\ominus}=199.4$ J mol^{-1} K^{-1}.

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) $T\approx374$ K.

17.17 (a) $q^R=660.6$; (b) $q^R=4.26\times10^4$.

17.23 $S=9.57\times10^{-15}$ J K^{-1}.

17.25 $G_m^{\ominus}-G_m^{\ominus}(0)=513.5$ kJ mol^{-1}.

17.27 At 10 K, $G_m^{\ominus}-G_m^{\ominus}(0)=660.8$ J mol^{-1}.
At 1000 K, $G_m^{\ominus}-G_m^{\ominus}(0)=241.5$ kJ mol^{-1}.

Chapter 18

18.1 (a) $\varepsilon=1.1\times10^8$ V m^{-1}; (b) $\varepsilon=4\times10^9$ V m^{-1}; (c) $\varepsilon=4$ kV m^{-1}.

18.3 $\alpha'=1.2\times10^{-23}$ cm^3, $\mu=0.86$ D.

18.5 $\alpha'=2.24\times10^{-24}$ cm^3, $\mu=1.58$ D, $P'_m=5.66$ cm^3 mol^{-1}, $\mu=1.58$ D.

18.7 (a) $\varepsilon=1.51\times10^{-23}$ J, $R_e=265$ pm.

18.9 $P_m = 8.14\ \mathrm{cm^3\ mol^{-1}}$, $\varepsilon_r = 1.76$, $n_r = 1.33$.

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

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

Chapter 19

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

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

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

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

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

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

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

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

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

19.17 (a) $R_g = \left(\dfrac{3}{5}\right)^{1/2} a$ (b) $R_g = \dfrac{l}{2\sqrt{3}}$. When M = 100 kg mol^{-1}, R_g/nm = 2.40. For a rod of radius 0.50 nm, $R_g = 46$ nm.

19.23 $v_p = 8v_{mol}$
For BSV, $B = 28\ \mathrm{m^3\ mol^{-1}}$. For Hb, $B = 0.33\ \mathrm{m^3\ mol^{-1}}$.

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

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

19.25 (a)

$\theta/°$	20	45	90
I_{rod}/I_{cc}	0.976	0.876	0.514

(b) 90°.

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

19.29 pH = 3.85.

Chapter 20

20.1 $\lambda = 118$ pm.

20.3 Yes, the data support.

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

20.7 a(KCl) = 628 pm, are broadly conistent.

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

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

20.15 $\rho = 1.385\ \mathrm{g\ cm^{-3}}$, $\rho o_s = 1.578\ \mathrm{g\ cm^{-3}}$.

20.17 0.736 eV.

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

20.21 $x = 0.41$.

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

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

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

Chapter 21

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

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

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

21.9 $\Lambda_m^\circ = 12.6\ \mathrm{mS\ m^2\ mol^{-1}}$; $\mathcal{K} = 7.30\ \mathrm{mS\ m^2\ mol^{-1}\ M^{-1/2}}$.
(a) $\Lambda_m = 11.96\ \mathrm{mS\ m^2\ mol^{-1}}$; (b) $\kappa = 119.6\ \mathrm{mS\ m^{-1}}$; (c) $R = 172.5\ \Omega$.

21.11 $s(\mathrm{Li^+}) = 4.0 \times 10^{-3}\ \mathrm{cm\ s^{-1}}$, $s(\mathrm{Na^+}) = 5.2 \times 10^{-3}\ \mathrm{cm\ s^{-1}}$; $s(\mathrm{K^+}) = 7.6 \times 10^{-3}\ \mathrm{cm\ s^{-1}}$.
$t(\mathrm{Li^+}) = 250$ s, $t(\mathrm{Na^+}) = 190$ s, $t(\mathrm{K^+}) = 130$ s.
(a) $d(\mathrm{Li^+}) = 1.3 \times 10^{-6}$ cm; $d(\mathrm{Na^+}) = 1.7 \times 10^{-6}$ cm; $d(\mathrm{K^+}) = 2.4 \times 10^{-6}$ cm.
(b) 43, 55 and 81 solvent molecule diameters respectively.

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

21.15 (a) 2.1×10^{-20} N molecule^{-1}; (b) 2.8×10^{-20} N molecule^{-1}; (c) 4.1×10^{-20} N molecule^{-1}.

21.17 9.3 kJ mol^{-1}.

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

21.21 (a) 3.68×10^{-10} m; (b) 3.07×10^{-10} m.

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

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

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

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

21.37 The total energy density (translational plus rotational) = ρT = 0.25 J cm^{-3}.

21.39 $t = 10^8$ s.

Chapter 22

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

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

22.5 9.70×10^4 J mol^{-1}.

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

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

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

22.13 rate = $kK_1K_2[\mathrm{HCl}]^3[\mathrm{CH_3CH{=}CH_2}]$; look for evidence of proposed intermediates, e.g. using infrared spectroscopy to search for $(\mathrm{HCl})_2$.

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

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

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

22.29 2720 y.

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

22.35 $v = k[\mathrm{A}][\mathrm{B}]$, $k = \dfrac{k_1k_2}{k_1'}$.

22.37 $E_a = 13.9$ kJ mol^{-1}, $A = 1.03 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

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

Chapter 23

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

$$\frac{\mathrm{d}[\mathrm{SiH_4}]}{\mathrm{d}t}=\left(\frac{k_1k_4k_5}{k_6}\right)^{1/2}[\mathrm{N_2O}][\mathrm{SiH_4}]^{1/2}$$

23.5 $\frac{\mathrm{d}[\mathrm{HI}]}{\mathrm{d}t}=\frac{2k_\mathrm{b}k_\mathrm{a}[\mathrm{I_2}][\mathrm{H_2}]}{k_\mathrm{a}'+k_\mathrm{b}[\mathrm{H_2}]}$. 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 $k_\mathrm{b}[\mathrm{H_2}]=k_\mathrm{a}'$ and hence, $\frac{\mathrm{d}[\mathrm{HI}]}{\mathrm{d}t}=2k_\mathrm{b}K[\mathrm{I_2}][\mathrm{H_2}]$.

23.7 (a) $\tau_0=6.67$ ns; (b) $k_\mathrm{f}=0.105\ \mathrm{ns^{-1}}$.

23.9 $k_q=1.98\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

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

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

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

23.21 $f=\frac{k_2k_4[\mathrm{CO}]}{k_2[\mathrm{CO}]+k_3[\mathrm{M}]}$.

23.27 Uncompetitive.

23.29 $R=2.6$ nm.

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

(b) $\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t}=-2k_\mathrm{a}[\mathrm{NO}]^2-2k_\mathrm{b}[\mathrm{O}][\mathrm{NO}]$;

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

(d) $E_\mathrm{a,eff}\approx381.39\ \mathrm{kJ\ mol^{-1}}$;

(e) $\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t}=-2k_\mathrm{b}\left(\frac{k_\mathrm{a}}{2k_\mathrm{d}[\mathrm{M}]}\right)^{1/2}[\mathrm{NO}]^2$;

(f) $\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t}=-2k_\mathrm{b}\left(\frac{k_\mathrm{a}}{2k_\mathrm{d}[\mathrm{M}]}\right)^{1/2}[\mathrm{NO}]^2$, where k_e is the rat constant for $\mathrm{NO}+\mathrm{O_2}\rightarrow\mathrm{O}+\mathrm{NO_2}$. $E_\mathrm{a,eff}=253\ \mathrm{kJ\ mol^{-1}}$, this value is consistent with the low range of the experimental values of $E_\mathrm{a,eff}$.

Chapter 24

24.1 (a) $\sigma^*=4.4\times10^{-20}\ \mathrm{m^2}$; (b) $P=0.15$.

24.3 $k_2=1.7\times10^{11}\ \mathrm{M^{-1}\ s^{-1}}$, $t=3.6$ ns.

24.5 2–.

24.9 (a) $-\frac{\mathrm{d}[\mathrm{F_2O}]}{\mathrm{d}t}=k_1[\mathrm{F_2O}]^2+k_2\left(\frac{k_1}{k_4}\right)^{1/2}[\mathrm{F_2O}]^{3/2}$; (b) $\Delta H(\mathrm{FO{-}F})\approx E_1=160.9\ \mathrm{kJ\ mol^{-1}}$, $\Delta H(\mathrm{O{-}F})\approx224.4\ \mathrm{kJ\ mol^{-1}}$, $E_2\approx60\ \mathrm{kJ\ mol^{-1}}$.

24.11 Linear regression analysis of ln(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 $P=5.2\times10^{-6}$.

24.17 $k_1=\frac{\upsilon^3}{\upsilon^{\ddagger 2}}\mathrm{e}^{-\beta\Delta E_0}$, (a) $D=2.7\times10^{-15}\ \mathrm{m^2\ s^{-1}}$, (b) $D=1.1\times10^{-14}\ \mathrm{m^2\ s^{-1}}$.

24.23 For $\mathrm{O_2}$ with ethyl: $P=1.6\times10^{-3}$; For $\mathrm{O_2}$ with cyclohexyl: $P=1.8\times10^{-3}$.

24.25 $z_\mathrm{A}=+3.0$.

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

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) $1.61\times10^{15}\ \mathrm{cm^{-2}}$; (b) $1.14\times10^{15}\ \mathrm{cm^{-2}}$; (c) $1.86\times10^{15}\ \mathrm{cm^{-2}}$.
For the collision frequencies:

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

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

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

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

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

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

25.15 $\delta=2.5\times10^{-4}$ 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 α.

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

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

(b) $k_\mathrm{a}=3.68\times10^{-3}$, $\Delta_\mathrm{ad}H=-8.67\ \mathrm{kJ\ mol^{-1}}$, $k_\mathrm{b}=2.62\times10^{-5}\ \mathrm{ppm^{-1}}$, $\Delta_\mathrm{b}H=-15.7\ \mathrm{kJ\ mol^{-1}}$.

(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: $(g_\mathrm{R}\ \mathrm{dm^{-3}})^{-1}$ [g_R = mass (grams) of rubber], K_F unit: $(\mathrm{mg})^{(1-1/n)}g_\mathrm{R}^{-1}\ \mathrm{dm}^{-3/n}$, K_L unit: $(\mathrm{mg\ dm^{-3}})^{-1}$, M unit: $(\mathrm{mg}\ g_\mathrm{R}^{-1})$.

(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) $q_\mathrm{rubber}/q_\mathrm{charcoal}=0.164c_\mathrm{eq}^{-0.46}$, 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 $0.28\ \mathrm{mg\ cm^{-2}d^{-1}}$.

Index

(T) denotes a table in the Data Section.

A

B

C

D

E

F

G

H

I

M

Q

R

S