

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

A3.10 Optical activity

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

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

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

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

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

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

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.

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 $^{-1}$.

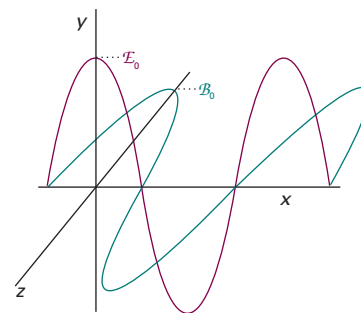


Fig. A3.7 Electromagnetic radiation consists of a wave of electric and magnetic fields perpendicular to the direction of propagation (in this case the x -direction), and mutually perpendicular to each other. This illustration shows a plane-polarized wave, with the electric and magnetic fields oscillating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

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

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

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

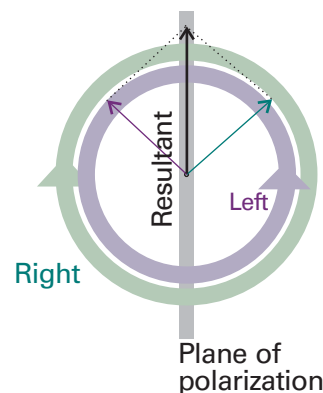


Fig. A3.8 The superposition of left and right circularly polarized light as viewed from an observer facing the oncoming beam.

A3.11 The Coulomb interaction

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

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

The constant ϵ_0 is the **vacuum permittivity**, a fundamental constant with the value $8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$. This very important relation is called the **Coulomb potential energy** and the interaction it describes is called the **Coulomb interaction** of two charges. The Coulomb potential energy is equal to the work that must be done to bring up a charge q_1 from infinity to a distance r from a charge q_2 .

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

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

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

In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**, 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 :

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

The units of potential are joules per coulomb, 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:

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

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

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

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

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

where $\nabla^2 = (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$. If the distribution is spherically symmetrical, then so too is 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:

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

A3.14 Electric current and power

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

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

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

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

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

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

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

Further reading

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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.

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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).
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- E: J. Emsley, *The elements*. Oxford University Press (1991).
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- TDOC: J.B. Pedley, J.D. Naylor, and S.P. Kirby, *Thermochemical data of organic compounds*. Chapman & Hall, London (1986).

Physical properties of selected materials

	$\rho/(\text{g cm}^{-3})$ at 293 K†	T_f/K	T_b/K		$\rho/(\text{g cm}^{-3})$ at 293 K†	T_f/K	T_b/K
Elements				Inorganic compounds			
Aluminium(s)	2.698	933.5	2740	CaCO ₃ (s, calcite)	2.71	1612	1171d
Argon(g)	1.381	83.8	87.3	CuSO ₄ ·5H ₂ O(s)	2.284	383(−H ₂ O)	423(−5H ₂ O)
Boron(s)	2.340	2573	3931	HBr(g)	2.77	184.3	206.4
Bromine(l)	3.123	265.9	331.9	HCl(g)	1.187	159.0	191.1
Carbon(s, gr)	2.260	3700s		HI(g)	2.85	222.4	237.8
Carbon(s, d)	3.513			H ₂ O(l)	0.997	273.2	373.2
Chlorine(g)	1.507	172.2	239.2	D ₂ O(l)	1.104	277.0	374.6
Copper(s)	8.960	1357	2840	NH ₃ (g)	0.817	195.4	238.8
Fluorine(g)	1.108	53.5	85.0	KBr(s)	2.750	1003	1708
Gold(s)	19.320	1338	3080	KCl(s)	1.984	1049	1773s
Helium(g)	0.125		4.22	NaCl(s)	2.165	1074	1686
Hydrogen(g)	0.071	14.0	20.3	H ₂ SO ₄ (l)	1.841	283.5	611.2
Iodine(s)	4.930	386.7	457.5				
Iron(s)	7.874	1808	3023	Organic compounds			
Krypton(g)	2.413	116.6	120.8	Acetaldehyde, CH ₃ CHO(l, g)	0.788	152	293
Lead(s)	11.350	600.6	2013	Acetic acid, CH ₃ COOH(l)	1.049	289.8	391
Lithium(s)	0.534	453.7	1620	Acetone, (CH ₃) ₂ CO(l)	0.787	178	329
Magnesium(s)	1.738	922.0	1363	Aniline, C ₆ H ₅ NH ₂ (l)	1.026	267	457
Mercury(l)	13.546	234.3	629.7	Anthracene, C ₁₄ H ₁₀ (s)	1.243	490	615
Neon(g)	1.207	24.5	27.1	Benzene, C ₆ H ₆ (l)	0.879	278.6	353.2
Nitrogen(g)	0.880	63.3	77.4	Carbon tetrachloride, CCl ₄ (l)	1.63	250	349.9
Oxygen(g)	1.140	54.8	90.2	Chloroform, CHCl ₃ (l)	1.499	209.6	334
Phosphorus(s, wh)	1.820	317.3	553	Ethanol, C ₂ H ₅ OH(l)	0.789	156	351.4
Potassium(s)	0.862	336.8	1047	Formaldehyde, HCHO(g)		181	254.0
Silver(s)	10.500	1235	2485	Glucose, C ₆ H ₁₂ O ₆ (s)	1.544	415	
Sodium(s)	0.971	371.0	1156	Methane, CH ₄ (g)		90.6	111.6
Sulfur(s, α)	2.070	386.0	717.8	Methanol, CH ₃ OH(l)	0.791	179.2	337.6
Uranium(s)	18.950	1406	4018	Naphthalene, C ₁₀ H ₈ (s)	1.145	353.4	491
Xenon(g)	2.939	161.3	166.1	Octane, C ₈ H ₁₈ (l)	0.703	216.4	398.8
Zinc(s)	7.133	692.7	1180	Phenol, C ₆ H ₅ OH(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	<i>m</i> /u	Abundance/%
H	¹ H	1.0078
	² H	0.015
He	³ He	0.000 13
	⁴ He	100
Li	⁶ Li	7.42
	⁷ Li	92.58
B	¹⁰ B	19.78
	¹¹ B	80.22
C	¹² C	98.89
	¹³ C	1.11
N	¹⁴ N	99.63
	¹⁵ N	0.37
O	¹⁶ O	99.76
	¹⁷ O	0.037
	¹⁸ O	0.204
F	¹⁹ F	100
P	³¹ P	100
S	³² S	95.0
	³³ S	0.76
	³⁴ S	4.22
Cl	³⁵ Cl	75.53
	³⁷ Cl	24.4
Br	⁷⁹ Br	50.54
	⁸¹ Br	49.46
I	¹²⁷ I	100

* Exact value.

Table 1.4 Second virial coefficients, *B*/(cm³ 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 cm⁶ mol^{−1}.

Table 1.5 Critical constants of gases

	<i>p</i> _c /atm	<i>V</i> _c /(cm ³ mol ^{−1})	<i>T</i> _c /K	<i>Z</i> _c	<i>T</i> _B /K
Ar	48.00	75.25	150.72	0.292	411.5
Br ₂	102	135	584	0.287	
C ₂ H ₄	50.50	124	283.1	0.270	
C ₂ H ₆	48.20	148	305.4	0.285	
C ₆ H 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 ₂ O	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

	$a/(\text{atm dm}^6 \text{ mol}^{-2})$	$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$		$a/(\text{atm dm}^6 \text{ mol}^{-2})$	$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$
Ar	1.337	3.20	H ₂ S	4.484	4.34
C ₂ H ₄	4.552	5.82	He	0.0341	2.38
C ₂ H ₆	5.507	6.51	Kr	5.125	1.06
C ₆ H 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 ₂ O	5.464	3.05			

Data: HCP.

Table 2.2 Temperature variation of molar heat capacities†

	a	$b/(10^{-3} \text{ K}^{-1})$	$c/(10^5 \text{ K}^2)$
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 ₂ O	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 $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = a + bT + c/T^2$.
Source: LR.

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

	T_f/K	Fusion	T_b/K	Vaporization		T_f/K	Fusion	T_b/K	Vaporization
Elements					CO ₂	217.0	8.33	194.6	25.23 s
Ag	1234	11.30	2436	250.6	CS ₂	161.2	4.39	319.4	26.74
Ar	83.81	1.188	87.29	6.506	H ₂ O	273.15	6.008	373.15	40.656
Br ₂	265.9	10.57	332.4	29.45					44.016 at 298 K
Cl ₂	172.1	6.41	239.1	20.41	H ₂ S	187.6	2.377	212.8	18.67
F ₂	53.6	0.26	85.0	3.16	H ₂ SO ₄	283.5	2.56		
H ₂	13.96	0.117	20.38	0.916	NH ₃	195.4	5.652	239.7	23.35
He	3.5	0.021	4.22	0.084	Organic compounds				
Hg	234.3	2.292	629.7	59.30	CH ₄	90.68	0.941	111.7	8.18
I ₂	386.8	15.52	458.4	41.80	CCl ₄	250.3	2.5	350	30.0
N ₂	63.15	0.719	77.35	5.586	C ₂ H ₆	89.85	2.86	184.6	14.7
Na	371.0	2.601	1156	98.01	C ₆ H ₆	278.61	10.59	353.2	30.8
O ₂	54.36	0.444	90.18	6.820	C ₆ H ₁₄	178	13.08	342.1	28.85
Xe	161	2.30	165	12.6	C ₁₀ H ₈	354	18.80	490.9	51.51
K	336.4	2.35	1031	80.23	CH ₃ OH	175.2	3.16	337.2	35.27
Inorganic compounds									37.99 at 298 K
CCl ₄	250.3	2.47	349.9	30.00	C ₂ H ₅ OH	158.7	4.60	352	43.5

Data: AIP; s denotes sublimation.

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

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$	$\Delta_c H^\circ/(\text{kJ mol}^{-1})$
C(s) (graphite)	12.011	0	0	5.740	8.527	−393.51
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113	−395.40
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 ₂ H ₂ (g), ethyne	26.04	+226.73	+209.20	200.94	43.93	−1300
C ₂ H ₄ (g), ethene	28.05	+52.26	+68.15	219.56	43.56	−1411
C ₂ H ₆ (g), ethane	30.07	−84.68	−32.82	229.60	52.63	−1560
C ₃ H ₆ (g), propene	42.08	+20.42	+62.78	267.05	63.89	−2058
C ₃ H ₆ (g), cyclopropane	42.08	+53.30	+104.45	237.55	55.94	−2091
C ₃ H ₈ (g), propane	44.10	−103.85	−23.49	269.91	73.5	−2220
C ₄ H ₈ (g), 1-butene	56.11	−0.13	+71.39	305.71	85.65	−2717
C ₄ H ₈ (g), <i>cis</i> -2-butene	56.11	−6.99	+65.95	300.94	78.91	−2710
C ₄ H ₈ (g), <i>trans</i> -2-butene	56.11	−11.17	+63.06	296.59	87.82	−2707
C ₄ H ₁₀ (g), butane	58.13	−126.15	−17.03	310.23	97.45	−2878
C ₅ H ₁₂ (g), pentane	72.15	−146.44	−8.20	348.40	120.2	−3537
C ₅ H ₁₂ (l)	72.15	−173.1				
C ₆ H ₆ (l), benzene	78.12	+49.0	+124.3	173.3	136.1	−3268

Table 2.5 (Continued)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$	$\Delta_c H^\circ/(\text{kJ mol}^{-1})$
Hydrocarbons (Continued)						
$\text{C}_6\text{H}_6(\text{g})$	78.12	+82.93	+129.72	269.31	81.67	−3302
$\text{C}_6\text{H}_{12}(\text{l})$, cyclohexane	84.16	−156	+26.8	204.4	156.5	−3920
$\text{C}_6\text{H}_{14}(\text{l})$, hexane	86.18	−198.7		204.3		−4163
$\text{C}_6\text{H}_5\text{CH}_3(\text{g})$, methylbenzene (toluene)	92.14	+50.0	+122.0	320.7	103.6	−3953
$\text{C}_7\text{H}_{16}(\text{l})$, heptane	100.21	−224.4	+1.0	328.6	224.3	
$\text{C}_8\text{H}_{18}(\text{l})$, octane	114.23	−249.9	+6.4	361.1		−5471
$\text{C}_8\text{H}_{18}(\text{l})$, iso-octane	114.23	−255.1				−5461
$\text{C}_{10}\text{H}_8(\text{s})$, naphthalene	128.18	+78.53				−5157
Alcohols and phenols						
$\text{CH}_3\text{OH}(\text{l})$, methanol	32.04	−238.66	−166.27	126.8	81.6	−726
$\text{CH}_3\text{OH}(\text{g})$	32.04	−200.66	−161.96	239.81	43.89	−764
$\text{C}_2\text{H}_5\text{OH}(\text{l})$, ethanol	46.07	−277.69	−174.78	160.7	111.46	−1368
$\text{C}_2\text{H}_5\text{OH}(\text{g})$	46.07	−235.10	−168.49	282.70	65.44	−1409
$\text{C}_6\text{H}_5\text{OH}(\text{s})$, phenol	94.12	−165.0	−50.9	146.0		−3054
Carboxylic acids, hydroxy acids, and esters						
$\text{HCOOH}(\text{l})$, formic	46.03	−424.72	−361.35	128.95	99.04	−255
$\text{CH}_3\text{COOH}(\text{l})$, acetic	60.05	−484.5	−389.9	159.8	124.3	−875
$\text{CH}_3\text{COOH}(\text{aq})$	60.05	−485.76	−396.46	178.7		
$\text{CH}_3\text{CO}_2^-(\text{aq})$	59.05	−486.01	−369.31	+86.6	−6.3	
$(\text{COOH})_2(\text{s})$, oxalic	90.04	−827.2			117	−254
$\text{C}_6\text{H}_5\text{COOH}(\text{s})$, benzoic	122.13	−385.1	−245.3	167.6	146.8	−3227
$\text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{s})$, lactic	90.08	−694.0				−1344
$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$, ethyl acetate	88.11	−479.0	−332.7	259.4	170.1	−2231
Alkanals and alkanones						
$\text{HCHO}(\text{g})$, methanal	30.03	−108.57	−102.53	218.77	35.40	−571
$\text{CH}_3\text{CHO}(\text{l})$, ethanal	44.05	−192.30	−128.12	160.2		−1166
$\text{CH}_3\text{CHO}(\text{g})$	44.05	−166.19	−128.86	250.3	57.3	−1192
$\text{CH}_3\text{COCH}_3(\text{l})$, propanone	58.08	−248.1	−155.4	200.4	124.7	−1790
Sugars						
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, α -D-glucose	180.16	−1274				−2808
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, β -D-glucose	180.16	−1268	−910	212		
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, β -D-fructose	180.16	−1266				−2810
$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$, sucrose	342.30	−2222	−1543	360.2		−5645
Nitrogen compounds						
$\text{CO}(\text{NH}_2)_2(\text{s})$, urea	60.06	−333.51	−197.33	104.60	93.14	−632
$\text{CH}_3\text{NH}_2(\text{g})$, methylamine	31.06	−22.97	+32.16	243.41	53.1	−1085
$\text{C}_6\text{H}_5\text{NH}_2(\text{l})$, aniline	93.13	+31.1				−3393
$\text{CH}_2(\text{NH}_2)\text{COOH}(\text{s})$, 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)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$
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 ₂ O 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)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$
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 ₂ CO 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)

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

Table 2.7 (Continued)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$
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 ₃ O ₄ (s) (magnetite)	231.54	-1118.4	-1015.4	146.4	143.43
Fe ₂ O 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 ₂ Cl 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)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$
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 ₂ O(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 ₂ O ₄ (g)	92.1	+9.16	+97.89	304.29	77.28
N ₂ O ₃ (s)	108.01	−43.1	+113.9	178.2	143.1
N ₂ O ₃ (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 ₂ OH(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 ₂ H ₄ (l)	32.05	+50.63	+149.43	121.21	139.3
NH ₄ NO ₃ (s)	80.04	−365.56	−183.87	151.08	84.1
NH ₄ Cl(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 ₃ PO ₃ (s)	82.00	−964.4			
H ₃ PO ₃ (aq)	82.00	−964.8			
H ₃ PO ₄ (s)	94.97	−1279.0	−1119.1	110.50	106.06
H ₃ PO ₄ (l)	94.97	−1266.9			
H ₃ PO ₄ (aq)	94.97	−1277.4	−1018.7	−222	

Table 2.7 (Continued)

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

Table 2.7 (Continued)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$
Sulfur (Continued)					
$\text{H}_2\text{SO}_4(\text{l})$	98.08	−813.99	−690.00	156.90	138.9
$\text{H}_2\text{SO}_4(\text{aq})$	98.08	−909.27	−744.53	20.1	−293
$\text{SO}_4^{2-}(\text{aq})$	96.06	−909.27	−744.53	+20.1	−293
$\text{HSO}_4^-(\text{aq})$	97.07	−887.34	−755.91	+131.8	−84
$\text{H}_2\text{S}(\text{g})$	34.08	−20.63	−33.56	205.79	34.23
$\text{H}_2\text{S}(\text{aq})$	34.08	−39.7	−27.83	121	
$\text{HS}^-(\text{aq})$	33.072	−17.6	+12.08	+62.08	
$\text{SF}_6(\text{g})$	146.05	−1209	−1105.3	291.82	97.28
Tin					
$\text{Sn}(\text{s}, \beta)$	118.69	0	0	51.55	26.99
$\text{Sn}(\text{g})$	118.69	+302.1	+267.3	168.49	20.26
$\text{Sn}^{2+}(\text{aq})$	118.69	−8.8	−27.2	−17	
$\text{SnO}(\text{s})$	134.69	−285.8	−256.9	56.5	44.31
$\text{SnO}_2(\text{s})$	150.69	−580.7	−519.6	52.3	52.59
Xenon					
$\text{Xe}(\text{g})$	131.30	0	0	169.68	20.786
Zinc					
$\text{Zn}(\text{s})$	65.37	0	0	41.63	25.40
$\text{Zn}(\text{g})$	65.37	+130.73	+95.14	160.98	20.79
$\text{Zn}^{2+}(\text{aq})$	65.37	−153.89	−147.06	−112.1	46
$\text{ZnO}(\text{s})$	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, $\Delta_{\text{hyd}} H^\circ/(\text{kJ mol}^{-1})$

	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 $\text{X}^+(\text{g}) + \text{Y}^-(\text{g}) \rightarrow \text{X}^+(\text{aq}) + \text{Y}^-(\text{aq})$.

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, $\Delta_{\text{hyd}} H^\circ/(\text{kJ mol}^{-1})$ 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 $\text{X}^\pm(\text{g}) \rightarrow \text{X}^\pm(\text{aq})$ based on $\text{H}^+(\text{g}) \rightarrow \text{H}^+(\text{aq})$; $\Delta H^\circ = -1090 \text{ kJ mol}^{-1}$.
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

	$\alpha/(10^{-4} \text{ K}^{-1})$	$\kappa_T/(10^{-6} \text{ atm}^{-1})$
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	$\mu_{JT}/(\text{K atm}^{-1})$
Air	603			0.189 at 50°C
Argon	723	83.8	87.3	
Carbon dioxide	1500	194.7s		1.11 at 300 K
Helium	40		4.22	−0.062
Hydrogen	202	14.0	20.3	−0.03
Krypton	1090	116.6	120.8	
Methane	968	90.6	111.6	
Neon	231	24.5	27.1	
Nitrogen	621	63.3	77.4	0.27
Oxygen	764	54.8	90.2	0.31

s: sublimes.
Data: AIP, JL, and M.W. Zemansky, *Heat and thermodynamics*. McGraw-Hill, New York (1957).

Table 3.1 Standard entropies (and temperatures) of phase transitions, $\Delta_{\text{trs}}S^\ominus/(\text{J K}^{-1} \text{ mol}^{-1})$

	Fusion (at T_f)	Vaporization (at T_b)
Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Br ₂	39.76 (at 265.9 K)	88.61 (at 332.4 K)
C ₆ H ₆	38.00 (at 278.6 K)	87.19 (at 353.2 K)
CH ₃ COOH	40.4 (at 289.8 K)	61.9 (at 391.4 K)
CH ₃ OH	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 ₂ O	22.00 (at 273.2 K)	109.0 (at 373.2 K)
H ₂ S	12.67 (at 187.6 K)	87.75 (at 212.0 K)
He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22 K)
N 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

	$\Delta_{\text{vap}} H^{\circ}/(\text{kJ mol}^{-1})$	$\theta_{\text{b}}/^{\circ}\text{C}$	$\Delta_{\text{vap}} S^{\circ}/(\text{J K}^{-1} \text{mol}^{-1})$
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, $K/(\text{kPa kg mol}^{-1})$

	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

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
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°	HCl	KCl	CaCl_2	H_2SO_4	LaCl_3	$\text{In}_2(\text{SO}_4)_3$
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°/V	Reduction half-reaction	E°/V
Strongly oxidizing		$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.16
$\text{H}_4\text{XeO}_6 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{XeO}_3 + 3\text{H}_2\text{O}$	+3.0	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87	$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	+0.07
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07	$\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	+2.05	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0, by definition
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	+1.98	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.78	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69	$\text{In}^+ + \text{e}^- \rightarrow \text{In}$	-0.14
$\text{Pb}^{4+} + 2\text{e}^- \rightarrow \text{Pb}^{2+}$	+1.67	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$2\text{HClO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.63	$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	-0.15
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	+1.61	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$2\text{HBrO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$	+1.60	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51	$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$	-0.34
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	+1.51	$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$	-0.34
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.40	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36	$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24	$\text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23	$\text{In}^{3+} + 2\text{e}^- \rightarrow \text{In}^+$	-0.44
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.09	$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.48
$\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$	+0.97	$\text{In}^{3+} + \text{e}^- \rightarrow \text{In}^{2+}$	-0.49
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96	$\text{U}^{4+} + \text{e}^- \rightarrow \text{U}^{3+}$	-0.61
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	+0.92	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.86	$\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81
$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	+0.80	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80	$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.91
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.79	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77	$\text{V}^{2+} + 2\text{e}^- \rightarrow \text{V}$	-1.19
$\text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}^- + 2\text{OH}^-$	+0.76	$\text{Ti}^{2+} + 2\text{e}^- \rightarrow \text{Ti}$	-1.63
$\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.62	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.60	$\text{U}^{3+} + 3\text{e}^- \rightarrow \text{U}$	-1.79
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	+0.56	$\text{Sc}^{3+} + 3\text{e}^- \rightarrow \text{Sc}$	-2.09
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.36
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52	$\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$	-2.48
$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.53	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.52
$\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	+0.49	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	+0.40	$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}$	-2.89
$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.91
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36	$\text{Ra}^{2+} + 2\text{e}^- \rightarrow \text{Ra}$	-2.92
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34	$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-2.92
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27	$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}$	-2.93
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$	+0.20	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05

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

Reduction half-reaction	E°/V	Reduction half-reaction	E°/V
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	+1.98	$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.53
$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	+0.0713	$\text{In}^+ + \text{e}^- \rightarrow \text{In}$	-0.14
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22	$\text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+$	-0.40
$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45	$\text{In}^{3+} + 2\text{e}^- \rightarrow \text{In}^+$	-0.44
$\text{AgF} + \text{e}^- \rightarrow \text{Ag} + \text{F}^-$	+0.78	$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$	-0.34
$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	-0.15	$\text{In}^{3+} + \text{e}^- \rightarrow \text{In}^{2+}$	-0.49
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.52
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.40	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	+2.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.36
$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}$	-1.85	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$	+0.20	$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	+1.51
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.09	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}^- + 2\text{OH}^-$	+0.76	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87	$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	+0.56
$\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81	$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.60
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$	-2.48	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	+1.61	$\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	+0.49
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36	$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	-0.80
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$	+0.10
$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	+0.40
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$	-0.56
$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.91	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74	$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-2.92	$\text{Pb}^{4+} + 2\text{e}^- \rightarrow \text{Pb}^{2+}$	+1.67
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34	$\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}$	+1.20
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.16	$\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$	+0.97
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87	$\text{Ra}^{2+} + 2\text{e}^- \rightarrow \text{Ra}$	-2.92
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44	$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}$	-2.93
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04	$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.48
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	+2.05
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36	$\text{Sc}^{3+} + 3\text{e}^- \rightarrow \text{Sc}$	-2.09
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0, by definition	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$2\text{HBrO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$	+1.60	$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}$	-2.89
$2\text{HClO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.63	$\text{Ti}^{2+} + 2\text{e}^- \rightarrow \text{Ti}$	-1.63
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.78	$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37
$\text{H}_4\text{XeO}_6 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{XeO}_3 + 3\text{H}_2\text{O}$	+3.0	$\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.79	$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$	-0.34
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27	$\text{U}^{3+} + 3\text{e}^- \rightarrow \text{U}$	-1.79
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.86	$\text{U}^{4+} + \text{e}^- \rightarrow \text{U}^{3+}$	-0.61
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	+0.92	$\text{V}^{2+} + 2\text{e}^- \rightarrow \text{V}$	-1.19
$\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.62	$\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$	-0.26
		$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-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 ₂ SO ₄	HSO ₄ ⁻	10 ²	-2
Perchloric*	HClO ₄	ClO ₄ ⁻	4.0 × 10 ¹	-1.6
Hydronium ion	H ₃ O ⁺	H ₂ O	1	0.0
Oxalic	(COOH) ₂	HOOCO ₂ ⁻	5.6 × 10 ⁻²	1.25
Sulfurous	H ₂ SO ₃	HSO ₃ ⁻	1.4 × 10 ⁻²	1.85
Hydrogensulfate ion	HSO ₄ ⁻	SO ₄ ²⁻	1.0 × 10 ⁻²	1.99
Phosphoric	H ₃ PO ₄	H ₂ PO ₄ ⁻	6.9 × 10 ⁻³	2.16
Glycinium ion	*NH ₃ CH ₂ COOH	NH ₂ CH ₂ COOH	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	HOOCO ₂ ⁻	C ₂ O ₄ ²⁻	1.5 × 10 ⁻⁵	3.81
Lactic	CH ₃ CH(OH)COOH	CH ₃ CH(OH)CO ₂ ⁻	1.4 × 10 ⁻⁴	3.86
Acetic (ethanoic)	CH ₃ COOH	CH ₃ CO ₂ ⁻	1.4 × 10 ⁻⁵	4.76
Butanoic	CH ₃ CH ₂ CH ₂ COOH	CH ₃ CH ₂ CH ₂ CO ₂ ⁻	1.5 × 10 ⁻⁵	4.83
Propanoic	CH ₃ CH ₂ COOH	CH ₃ CH ₂ CO ₂ ⁻	1.4 × 10 ⁻⁵	4.87
Anilinium ion	C ₆ H ₅ NH ₃ ⁺	C ₆ H ₅ NH ₂	1.3 × 10 ⁻⁵	4.87
Pyridinium ion	C ₅ H ₅ NH ⁺	C ₅ H ₅ N	5.9 × 10 ⁻⁶	5.23
Carbonic	H ₂ CO ₃	HCO ₃ ⁻	4.5 × 10 ⁻⁷	6.35
Hydrosulfuric	H ₂ S	HS ⁻	8.9 × 10 ⁻⁸	7.05
Dihydrogenphosphate ion	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.2 × 10 ⁻⁸	7.21
Hypochlorous	HClO	ClO ⁻	4.0 × 10 ⁻⁸	7.40
Hydrazinium ion	NH ₂ NH ₃ ⁺	NH ₂ NH 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) ₃ NH ⁺	(CH ₃) ₃ N	1.6 × 10 ⁻¹⁰	9.80
Phenol	C ₆ H ₅ OH	C ₆ H ₅ O ⁻	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 ₃ CH ₂ NH ₃ ⁺	CH ₃ CH ₂ NH ₂	2.2 × 10 ⁻¹¹	10.65
Methylammonium ion	CH ₃ NH ₃ ⁺	CH ₃ NH ₂	2.2 × 10 ⁻¹¹	10.66
Dimethylammonium ion	(CH ₃) ₂ NH ₂ ⁺	(CH ₃) ₂ NH	1.9 × 10 ⁻¹¹	10.73
Triethylammonium ion	(CH ₃ CH ₂) ₃ NH ⁺	(CH ₃ CH ₂) ₃ N	1.8 × 10 ⁻¹¹	10.75
Diethylammonium ion	(CH ₃ CH ₂) ₂ NH ₂ ⁺	(CH ₃ CH ₂) ₂ NH	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 ₃ COOH	CH ₃ CO ₂ ⁻	1.4 × 10 ⁻⁵	4.76
Ammonium ion	NH ₄ ⁺	NH ₃	5.6 × 10 ⁻¹⁰	9.25
Anilinium ion	C ₆ H ₅ NH ₃ ⁺	C ₆ H ₅ NH ₂	1.3 × 10 ⁻⁵	4.87
Boric*	B(OH) ₃	B(OH) ₄ ⁻	5.4 × 10 ⁻¹⁰	9.27
Butanoic	CH ₃ CH ₂ CH ₂ COOH	CH ₃ CH ₂ CH ₂ CO ₂ ⁻	1.5 × 10 ⁻⁵	4.83
Carbonic	H ₂ CO ₃	HCO ₃ ⁻	4.5 × 10 ⁻⁷	6.35
Diethylammonium ion	(CH ₃ CH ₂) ₂ NH ₂ ⁺	(CH ₃ CH ₂) ₂ NH	1.4 × 10 ⁻¹¹	10.84
Dihydrogenphosphate ion	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.2 × 10 ⁻⁸	7.21
Dimethylammonium ion	(CH ₃) ₂ NH ₂ ⁺	(CH ₃) ₂ NH	1.9 × 10 ⁻¹¹	10.73
Ethylammonium ion	CH ₃ CH ₂ NH ₃ ⁺	CH ₃ CH ₂ NH ₂	2.2 × 10 ⁻¹¹	10.65
Formic	HCOOH	HCO ₂ ⁻	1.8 × 10 ⁻⁴	3.75
Glycinium ion	⁺ NH ₃ CH ₂ COOH	NH ₂ CH ₂ COOH	4.5 × 10 ⁻³	2.35
Hydrazinium ion	NH ₂ NH ₃ ⁺	NH ₂ NH 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	HOOC-CO ₂ ⁻	C ₂ O 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 ₃ O ⁺	H ₂ O	1	0.0
Hydrosulfuric	H ₂ S	HS ⁻	8.9 × 10 ⁻⁸	7.05
Hypobromous	HBrO	BrO ⁻	2.8 × 10 ⁻⁹	8.55
Hypochlorous	HOCl	ClO ⁻	4.0 × 10 ⁻⁸	7.40
Hypoiodous	HIO	IO ⁻	3 × 10 ⁻¹¹	10.5
Lactic	CH ₃ CH(OH)COOH	CH ₃ CH(OH)CO ₂ ⁻	1.4 × 10 ⁻⁴	3.86
Methylammonium ion	CH ₃ NH ₃ ⁺	CH ₃ NH ₂	2.2 × 10 ⁻¹¹	10.66
Oxalic	(COOH) ₂	HOOC-CO ₂ ⁻	5.6 × 10 ⁻²	1.25
Perchloric*	HClO ₄	ClO ₄ ⁻	4.0 × 10 ¹	-1.6
Phenol	C ₆ H ₅ OH	C ₆ H ₅ O ⁻	1.0 × 10 ⁻¹⁰	9.99
Phosphoric	H ₃ PO ₄	H ₂ PO ₄ ⁻	6.9 × 10 ⁻³	2.16
Propanoic	CH ₃ CH ₂ COOH	CH ₃ CH ₂ CO ₂ ⁻	1.4 × 10 ⁻⁵	4.87
Pyridinium ion	C ₅ H ₅ NH ⁺	C ₅ H ₅ N	5.9 × 10 ⁻⁶	5.23
Sulfuric	H ₂ SO ₄	HSO ₄ ⁻	10 ²	-2
Sulfurous	H ₂ SO ₃	HSO ₃ ⁻	1.4 × 10 ⁻²	1.85
Triethylammonium ion	(CH ₃ CH ₂) ₃ NH ⁺	(CH ₃ CH ₂) ₃ N	1.8 × 10 ⁻¹¹	10.75
Trimethylammonium ion	(CH ₃) ₃ NH ⁺	(CH ₃) ₃ N	1.6 × 10 ⁻¹⁰	9.80

* At 293 K.

Table 9.2 The error function

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

Data: AS.

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

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

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

Data: E.

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

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

Data: E.

Table 11.2 Bond lengths, R_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, $\Delta H^\circ(\text{A–B})/(\text{kJ mol}^{-1})$ 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 ₆ H ₅	469
H ₃ C–CH ₃	368	H ₂ C=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 ₂ N–NO ₂	54		

Data: HCP, KL.

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

	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C	412	348(i) 612(ii) 838(iii) 518(a)									
N	388	305(i) 613(ii) 890(iii)	163(i) 409(ii) 946(iii)								
O	463	360(i) 743(ii)	157	146(i) 497(ii)							
F	565	484	270	185	155						
Cl	431	338	200	203	254	242					
Br	366	276				219	193				
I	299	238				210	178	151			
S	338	259			496	250	212		264		
P	322									201	
Si	318		374	466							226

(i) Single bond, (ii) double bond, (iii) triple bond, (a) aromatic.
Data: HCP and L. Pauling, *The nature of the chemical bond*. Cornell University Press (1960).

Table 11.4 Pauling (*italics*) and Mulliken electronegativities

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

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

Table 13.2 Properties of diatomic molecules

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

Data: AIP.

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

C—H stretch	2850–2960
C—H bend	1340–1465
C—C stretch, bend	700–1250
C=C stretch	1620–1680
C≡C stretch	2100–2260
O—H stretch	3590–3650
H-bonds	3200–3570
C=O stretch	1640–1780
C≡N stretch	2215–2275
N—H stretch	3200–3500
C—F stretch	1000–1400
C—Cl stretch	600–800
C—Br stretch	500–600
C—I stretch	500
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	$\nu/(10^{14} \text{ Hz})$	$\tilde{\nu}/(10^4 \text{ cm}^{-1})$	E/eV	$E/(\text{kJ mol}^{-1})$
Infrared	>1000	<3.00	<1.00	<1.24	<120
Red	700	4.28	1.43	1.77	171
Orange	620	4.84	1.61	2.00	193
Yellow	580	5.17	1.72	2.14	206
Green	530	5.66	1.89	2.34	226
Blue	470	6.38	2.13	2.64	254
Violet	420	7.14	2.38	2.95	285
Near ultraviolet	300	10.0	3.33	4.15	400
Far ultraviolet	<200	>15.0	>5.00	>6.20	>598

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

Table 14.3 Absorption characteristics of some groups and molecules

Group	$\bar{\nu}_{\max}/(10^4 \text{ cm}^{-1})$	λ_{\max}/nm	$\epsilon_{\max}/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
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
–NO ₂	>3.9	<260	Strong
	3.6	280	10
	4.8	210	1.0×10^4
C ₆ H 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 ₂ O ($\pi^* \leftarrow n$)	6.0	167	7.0×10^3

Table 15.2 Nuclear spin properties

Nuclide	Natural abundance %	Spin <i>I</i>	Magnetic moment μ/μ_{N}	<i>g</i> -value	$\gamma/(10^7 \text{ T}^{-1} \text{ s}^{-1})$	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 ; $\mu = g_I \mu_{\text{N}} I$ 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(2 <i>p</i>)
¹⁴ N	1	55.2(2s)	4.8(2 <i>p</i>)
¹⁹ F	$\frac{1}{2}$	1720(2s)	108.4(2 <i>p</i>)
³¹ P	$\frac{1}{2}$	364(3s)	20.6(3 <i>p</i>)
³⁵ Cl	$\frac{3}{2}$	168(3s)	10.0(3 <i>p</i>)
³⁷ Cl	$\frac{3}{2}$	140(3s)	8.4(3 <i>p</i>)

Data: P.W. Atkins and M.C.R. Symons, *The structure of inorganic radicals*. Elsevier, Amsterdam (1967).

Table 18.1 Dipole moments, polarizabilities, and polarizability volumes

	$\mu/(10^{-30} \text{ C m})$	μ/D	$\alpha/(10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2)$	$\alpha'/(10^{-30} \text{ m}^3)$
Ar	0	0	1.66	1.85
C ₂ H ₅ OH	5.64	1.69		
C ₆ H ₅ CH ₃	1.20	0.36		
C ₆ H ₆	0	0	10.4	11.6
CCl ₄	0	0	10.3	11.7
CH ₂ Cl ₂	5.24	1.57	6.80	7.57
CH ₃ Cl	6.24	1.87	4.53	5.04
CH ₃ OH	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 ₂ O	6.17	1.85	1.48	1.65
HBr	2.67	0.80	3.61	4.01
HCl	3.60	1.08	2.63	2.93
He	0	0	0.20	0.22
HF	6.37	1.91	0.51	0.57
HI	1.40	0.42	5.45	6.06
N ₂	0	0	1.77	1.97
NH ₃	4.90	1.47	2.22	2.47
1,2-C ₆ H 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

	$(\epsilon/k)/K$	r_0/pm
Ar	111.84	362.3
C ₂ H ₂	209.11	463.5
C ₂ H ₄	200.78	458.9
C ₂ H ₆	216.12	478.2
C ₆ H 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

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

Data: KL.

Table 19.1 Radius of gyration of some macromolecules

	$M/(\text{kg mol}^{-1})$	R_g/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

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

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

Table 19.3 Frictional coefficients and molecular geometry

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

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

Sphere; radius a , $c = af_0$

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

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

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

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

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

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

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

Table 19.4 Intrinsic viscosity

Macromolecule	Solvent	$\theta/^\circ\text{C}$	$K/(10^{-3} \text{ cm}^3 \text{ g}^{-1})$	a
Polystyrene	Benzene	25	9.5	0.74
	Cyclohexane	34†	81	0.50
Polyisobutylene	Benzene	23†	83	0.50
	Cyclohexane	30	26	0.70
Amylose	0.33 M KCl(aq)	25†	113	0.50
Various proteins‡	Guanidine hydrochloride + HSCH ₂ CH ₂ OH		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 $\text{MX}(\text{s}) \rightarrow \text{M}^+(\text{g}) + \text{X}^-(\text{g})$.
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
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$	+176	+192
$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$	+2640	$+2.79 \times 10^3$
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$	+416	+600
$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$	+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, $\eta/(10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$

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

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

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

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

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

Convert $\text{kg m}^{-1} \text{ s}^{-1}$ 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, $\lambda/(\text{mS m}^2 \text{ mol}^{-1})$

Cations		Anions	
Ba ²⁺	12.72	Br ⁻	7.81
Ca ²⁺	11.90	CH ₃ CO 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 ₂ H 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, $u/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$

Cations		Anions	
Ag ⁺	6.24	Br ⁻	8.09
Ca ²⁺	6.17	CH ₃ CO 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	$A/(\text{mS m}^2 \text{ mol}^{-1}/(\text{mol dm}^{-3})^{1/2})$	$B/(\text{mol dm}^{-3})^{-1/2}$
Acetone (propanone)	3.28	1.63
Acetonitrile	2.29	0.716
Ethanol	8.97	1.83
Methanol	15.61	0.923
Nitrobenzene	4.42	0.776
Nitromethane	111	0.708
Water	6.020	0.229

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

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

Molecules in liquids				Ions in water			
I 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 ₂ O in water	2.26				
		CH ₃ OH in water	1.58				
		C ₂ H ₅ OH in water	1.24				

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

Table 22.1 Kinetic data for first-order reactions

	Phase	$\theta/^\circ\text{C}$	k/s^{-1}	$t_{1/2}$
$2 \text{ N}_2\text{O}_5 \rightarrow 4 \text{ NO}_2 + \text{O}_2$	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
$\text{C}_2\text{H}_6 \rightarrow 2 \text{ CH}_3$	g	700	5.36×10^{-4}	21.6 min
Cyclopropane \rightarrow propene	g	500	6.71×10^{-4}	17.2 min
$\text{CH}_3\text{N}_2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{N}_2$	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	$\theta/^\circ\text{C}$	$k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
$2 \text{ NOBr} \rightarrow 2 \text{ NO} + \text{Br}_2$	g	10	0.80
$2 \text{ NO}_2 \rightarrow 2 \text{ NO} + \text{O}_2$	g	300	0.54
$\text{H}_2 + \text{I}_2 \rightarrow 2 \text{ HI}$	g	400	2.42×10^{-2}
$\text{D}_2 + \text{HCl} \rightarrow \text{DH} + \text{DCl}$	g	600	0.141
$2 \text{ I} \rightarrow \text{I}_2$	g	23	7×10^9
	hexane	50	1.8×10^{10}
$\text{CH}_3\text{Cl} + \text{CH}_3\text{O}^-$	methanol	20	2.29×10^{-6}
$\text{CH}_3\text{Br} + \text{CH}_3\text{O}^-$	methanol	20	9.23×10^{-6}
$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	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}	$E_a/(kJ\ mol^{-1})$
Cyclopropane \rightarrow propene	1.58×10^{15}	272
$CH_3NC \rightarrow CH_3CN$	3.98×10^{13}	160
<i>cis</i> -CHD=CHD \rightarrow <i>trans</i> -CHD=CHD	3.16×10^{12}	256
Cyclobutane \rightarrow 2 C ₂ H ₄	3.98×10^{13}	261
C ₂ H ₅ I \rightarrow C ₂ H ₄ + HI	2.51×10^{17}	209
C ₂ H ₆ \rightarrow 2 CH ₃	2.51×10^7	384
2 N ₂ O ₅ \rightarrow 4 NO ₂ + O ₂	4.94×10^{13}	103
N ₂ O \rightarrow N ₂ + O	7.94×10^{11}	250
C ₂ H ₅ \rightarrow C ₂ H ₄ + H	1.0×10^{13}	167
Second-order, gas-phase	$A/(dm^3\ mol^{-1}\ s^{-1})$	$E_a/(kJ\ mol^{-1})$
O + N ₂ \rightarrow NO + N	1×10^{11}	315
OH + H ₂ \rightarrow H ₂ O + H	8×10^{10}	42
Cl + H ₂ \rightarrow HCl + H	8×10^{10}	23
2 CH ₃ \rightarrow C ₂ H 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 ₂ H ₆ \rightarrow CH ₄ + C ₂ H ₅	2×10^8	44
C ₆ H ₅ + H ₂ \rightarrow C ₆ H ₆ + H	1×10^8	ca. 25
Second-order, solution	$A/(dm^3\ mol^{-1}\ s^{-1})$	$E_a/(kJ\ mol^{-1})$
C ₂ H ₅ ONa + CH ₃ I in ethanol	2.42×10^{11}	81.6
C ₂ H ₅ Br + OH ⁻ in water	4.30×10^{11}	89.5
C ₂ H ₅ I + C ₂ H ₅ O ⁻ in ethanol	1.49×10^{11}	86.6
CH ₃ I + C ₂ H ₅ O ⁻ in ethanol	2.42×10^{11}	81.6
C ₂ H ₅ Br + OH ⁻ in ethanol	4.30×10^{11}	89.5
CO ₂ + OH ⁻ in water	1.5×10^{10}	38
CH ₃ I + S ₂ O ₃ ²⁻ in water	2.19×10^{12}	78.7
Sucrose + H ₂ O in acidic water	1.50×10^{15}	107.9
(CH ₃) ₃ CCl 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 ₆ H ₅ NH ₂ + C ₆ H ₅ COCH ₂ Br		
in benzene	91	34

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

Table 24.1 Arrhenius parameters for gas-phase reactions

	$A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$		$E_a/(\text{kJ mol}^{-1})$	P
	Experiment	Theory		
$2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$	9.4×10^9	5.9×10^{10}	102.0	0.16
$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$	2.0×10^9	4.0×10^{10}	111.0	5.0×10^{-2}
$2 \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	6.3×10^7	2.5×10^{10}	0.0	2.5×10^{-3}
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	1.24×10^6	7.4×10^{11}	180	1.7×10^{-6}
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	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, $\Delta_{\text{ad}}H^\ominus/(\text{kJ mol}^{-1})$

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, $\Delta_{\text{ad}}H^\ominus/(\text{kJ mol}^{-1})$

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	$E_a/(\text{kJ mol}^{-1})$
$2 \text{ HI} \rightarrow \text{H}_2 + \text{I}_2$	None	184
	Au(s)	105
	Pt(s)	59
$2 \text{ NH}_3 \rightarrow \text{N}_2 + 3 \text{ H}_2$	None	350
	W(s)	162
$2 \text{ N}_2\text{O} \rightarrow 2 \text{ N}_2 + \text{O}_2$	None	245
	Au(s)	121
	Pt(s)	134
$(\text{C}_2\text{H}_5)_2\text{O}$ pyrolysis	None	224
	$\text{I}_2(\text{g})$	144

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

Table 25.6 Exchange current densities and transfer coefficients at 298 K

Reaction	Electrode	$j_0/(\text{A cm}^{-2})$	α
$2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{H}_2$	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}	
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	Pt	2.5×10^{-3}	0.58
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	Pt	4.0×10^{-5}	0.75

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

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.

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	$2C_5$	$2C_5^2$	$5\sigma_v$	$h = 10, \alpha = 72^\circ$	
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	$2C_\phi^\dagger$	$\infty\sigma_v$	$h = \infty$	
$A_1(\Sigma^+)$	1	1	1	$z, z^2, x^2 + y^2$	
$A_2(\Sigma^-)$	1	1	-1		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)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	(R_x, R_y)
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	$2S_5$	$2S_5^3$	$5\sigma_v$	$h = 20$	$\alpha = 72^\circ$
A'_1	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$	
A'_2	1	1	1	-1	1	1	1	-1	R_z	
E'_1	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	(x, y)	
E'_2	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	$(x^2 - y^2, xy)$	
A''_1	1	1	1	1	-1	-1	-1	-1		
A''_2	1	1	1	-1	-1	-1	-1	1	z	
E''_1	2	$2 \cos \alpha$	$2 \cos 2\alpha$	0	-2	$-2 \cos \alpha$	$-2 \cos 2\alpha$	0	(xz, yz)	(R_x, R_y)
E''_2	2	$2 \cos 2\alpha$	$2 \cos \alpha$	0	-2	$-2 \cos 2\alpha$	$-2 \cos \alpha$	0		

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

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	$(x, y, z), (xy, xz, yz)$

$O_h (m\bar{3}m)$	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, xz)
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	$z^2 + y^2 + x^2$
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 $R = 0.082\,061\,5\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}$, $M = 31.9987\,\text{g}\,\text{mol}^{-1}$.
1.8 P_4 .
1.9 2.61 kg.
1.10 (a) $3.14\,\text{dm}^3$; (b) 28.2 kPa.
1.11 $16.14\,\text{g}\,\text{mol}^{-1}$.
1.12 -270°C .
1.13 (a) (i) 1.0 atm, (ii) 270 atm.
(b) (i) 0.99 atm, (ii) 190 atm.
1.14 $a = 1.34 \times 10^{-1}\,\text{kg}\,\text{m}^5\,\text{s}^{-2}\,\text{mol}^{-2}$, $b = 4.36 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$.
1.15 (a) 1.12, repulsive; (b) $2.7\,\text{dm}^3\,\text{mol}^{-1}$.
1.16 (a) $0.124\,\text{dm}^3\,\text{mol}^{-1}$; (b) $0.112\,\text{dm}^3\,\text{mol}^{-1}$.
1.17 (a) $8.7\,\text{cm}^3$; (b) $-0.15\,\text{dm}^3\,\text{mol}^{-1}$.
1.18 (a) $x_N = 0.63$, $x_H = 0.37$;
(b) $p_N = 2.5\,\text{atm}$, $p_H = 1.5\,\text{atm}$;
(c) 4.0 atm.
1.19 $b = 0.0493\,\text{dm}^3\,\text{mol}^{-1}$, $r = 1.94 \times 10^{-10}\,\text{m}$, $a = 3.16\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}$.
1.20 (a) 1259 K; (b) 0.129 nm.
1.21 (a) $p = 2.6\,\text{atm}$, $T = 881\,\text{K}$;
(b) $p = 2.2\,\text{atm}$, $T = 718\,\text{K}$;
(c) $p = 1.4\,\text{atm}$, $T = 356\,\text{K}$.
1.22 $b = 1.3 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}$, $Z = 0.67$.

Chapter 2

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

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

Chapter 3

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

Chapter 4

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

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

Chapter 5

- 5.1 843.5 cm^3 .
 5.2 18 cm^3 .
 5.3 $8.2 \times 10^3 \text{ kPa}$.
 5.4 $1.5 \times 10^2 \text{ kPa}$.
 5.5 270 g mol^{-1} .
 5.6 178 g mol^{-1} .
 5.7 -0.077°C .
 5.8 $\Delta_{\text{mix}}G = -17.3 \text{ J}$, $\Delta_{\text{mix}}S = 6.34 \times 10^{-2} \text{ J K}^{-1}$.
 5.9 $\Delta_{\text{mix}}G = -3.43 \text{ kJ}$, $\Delta_{\text{mix}}S = +11.5 \text{ J K}^{-1}$, $\Delta_{\text{mix}}H = 0$.
 5.10 (a) 1:1; (b) 0.7358.
 5.11 N_2 : $0.51 \text{ mmol kg}^{-1}$, O_2 : $0.27 \text{ mmol kg}^{-1}$.
 5.12 $0.067 \text{ mol dm}^{-3}$.
 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) $38.8 \text{ g Ba(NO}_3)_2$.
 5.20 0.661.
 5.21 1.3.

Chapter 6

- 6.1 $x_A = 0.5$, $y_B = 0.5$.
 6.2 $x_A = 0.653$, $x_B = 0.347$, $p = 73.4 \text{ kPa}$.
 6.3 (a) the solution is ideal; (b) $\gamma_A = 0.4582$, $\gamma_B = 0.5418$.
 6.4 (a) 6.4 kPa ; (b) $\gamma_B = 0.77$, $\gamma_T = 0.23$; (c) $p(\text{final}) = 4.5 \text{ kPa}$.
 6.5 (a) $\gamma_A = 0.81$; (b) $x_A = 0.67$, $\gamma_A = 0.925$.
 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) $x_{\text{AB}_2} \approx 0.8$; (c) $x_{\text{AB}_2} \approx 0.6$.
 6.14 A solid solution with $x(\text{ZrF}_4) = 0.24$ appears at 855°C . The solid solution continues to form, and its ZrF_4 content increases until it reaches $x(\text{ZrF}_4) = 0.40$ and 820°C . At that temperature, the entire sample is solid.
 6.17 (a) When x_A falls to 0.47, a second liquid phase appears. The amount of new phase increases as x_A falls and the amount of original phase decreases until, at $x_A = 0.314$, only one liquid remains.
 (b) The mixture has a single liquid phase at all compositions.

Chapter 7

- 7.1 (a) $\Delta_r G = 0$; (b) $K = 0.16841$; (c) $\Delta_r G^\circ = 4.41 \text{ kJ mol}^{-1}$.
 7.2 (a) $K = 0.24$; (b) $\Delta_r G^\circ = 19 \text{ kJ mol}^{-1}$; (c) $K = 2.96$.

- 7.3 (a) $K = 1.3 \times 10^{54}$, $\Delta_r G^\circ = 308.84 \text{ kJ mol}^{-1}$;
 (b) $K = 3.5 \times 10^{49}$, $\Delta_r G^\circ = -306.52 \text{ kJ mol}^{-1}$.
 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) $\Delta_r G^\circ = -5.6 \text{ kJ mol}^{-1}$.
 7.5 $T_2 = 1.4 \times 10^3 \text{ K}$.
 7.6 $\Delta_r H^\circ = 7.191 \text{ kJ mol}^{-1}$, $\Delta_r S^\circ = -21 \text{ J K}^{-1} \text{ mol}^{-1}$.
 7.7 $\Delta G^\circ = -41.0 \text{ kJ mol}^{-1}$.
 7.9 $x_{\text{NO}} = 1.6 \times 10^{-2}$.
 7.10 (a) $\Delta_r H^\circ = 39 \text{ kJ mol}^{-1}$; (b) $\Delta_r H^\circ = -39 \text{ kJ mol}^{-1}$.
 7.11 (a) At 427°C , $K = 9.24$, At 459°C , $K = 31.08$;
 (b) $\Delta_r G^\circ = -12.9 \text{ kJ mol}^{-1}$;
 (c) $\Delta_r H^\circ = +161 \text{ kJ mol}^{-1}$;
 (d) $\Delta_r S^\circ = +248 \text{ J K}^{-1} \text{ mol}^{-1}$.
 7.12 $T = 397 \text{ K}$.
 7.13 $\Delta_r G^\circ = -128.8 \text{ kJ mol}^{-1}$.
 7.14 (a) R: $\text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq})$ +0.45 V
 L: $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$ +1.36 V
 Overall (R – L): $\text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq}) + \text{Cl}_2(\text{g})$ -0.91 V
 (b) R: $\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$ +0.15 V
 L: $2\text{Fe}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}(\text{aq})$ +0.77 V
 Overall (R – L): $\text{Sn}^{4+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$ -0.62 V
 (c) R: $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$ +1.23 V
 L: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ +0.34 V
 Overall (R – L): $\text{Cu}(\text{s}) + \text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ +0.89 V
 7.15 (a) R: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$ -0.83 V
 L: $2\text{Na}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Na}(\text{s})$ -2.71 V
 and the cell is $\text{Na}(\text{s}) | \text{Na}^+(\text{aq}), \text{OH}^-(\text{aq}) | \text{H}_2(\text{g}) | \text{Pt}$ +1.88 V
 (b) R: $\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$ +0.54 V
 L: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ 0.00 V
 and the cell is $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq}), \text{I}^-(\text{aq}) | \text{I}_2(\text{s}) | \text{Pt}$ +0.54 V
 (c) R: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ 0.00 V
 L: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ 0.083 V
 and the cell is $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq}), \text{OH}^-(\text{aq}) | \text{H}_2(\text{g}) | \text{Pt}$ 0.083 V
 7.16 (a) $E = E^\circ - \frac{2RT}{F} \ln(\gamma_{\pm} b)$; (b) $\Delta_r G^\circ = -89.89 \text{ kJ mol}^{-1}$;
 (c) $E^\circ = +0.223 \text{ V}$.
 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 $v = 1.3 \times 10^{-5} \text{ m s}^{-1}$.
 8.2 $p = 1.89 \times 10^{-27} \text{ kg m s}^{-1}$, $v = 0.565 \text{ m s}^{-1}$.
 8.3 $\Delta x = 5.8 \times 10^{-6} \text{ m}$.
 8.4 (a) $E = 0.93 \times 10^{-19} \text{ J}$, E (per mole) = 598 kJ mol^{-1} ;
 (b) $E = 1.32 \times 10^{-15} \text{ J}$, E (per mole) = $7.98 \times 10^5 \text{ kJ mol}^{-1}$;
 (c) $E = 1.99 \times 10^{-23} \text{ J}$, E (per mole) = $0.012 \text{ kJ mol}^{-1}$.
 8.5 (a) $v = 0.499 \text{ m s}^{-1}$; (b) $v = 665 \text{ m s}^{-1}$; (c) $v = 9.98 \times 10^{-6} \text{ m s}^{-1}$.
 8.6 $v = 158 \text{ m s}^{-1}$.
 8.7 (a) $3.52 \times 10^{17} \text{ s}^{-1}$; (b) $3.52 \times 10^{18} \text{ s}^{-1}$.
 8.8 (a) 0; (b) $E_K = 6.84 \times 10^{-19} \text{ J}$; $v = 1.23 \times 10^6 \text{ m s}^{-1}$.
 8.9 (a) $E = 2.65 \times 10^{-19} \text{ J}$, or 160 kJ mol^{-1} ; (b) $E = 3.00 \times 10^{-19} \text{ J}$, or 181 kJ mol^{-1} ; (c) $E = 6.62 \times 10^{-31} \text{ J}$, or $4.0 \times 10^{-10} \text{ kJ mol}^{-1}$.
 8.10 (a) $\lambda = 1.23 \times 10^{-10} \text{ m}$; (b) $\lambda = 3.9 \times 10^{-11} \text{ m}$; (c) $\lambda = 3.88 \times 10^{-11} \text{ m}$.
 8.12 $\Delta x = 100 \text{ pm}$, speed (Δv): $5.8 \times 10^5 \text{ m s}^{-1}$.

8.13 $1.67 \times 10^{-16} \text{ J}$.

8.14 \hbar .

Chapter 9

9.1 (a) $2.14 \times 10^{-19} \text{ J}$, 1.34 eV , $1.08 \times 10^4 \text{ cm}^{-1}$, 129 kJ mol^{-1} ;

(b) $3.48 \times 10^{-19} \text{ J}$, 2.17 eV , $1.75 \times 10^4 \text{ cm}^{-1}$, 210 kJ mol^{-1} .

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

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

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

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

9.6 6.

9.7 $n = 7.26 \times 10^{10}$, $\Delta E = 1.71 \times 10^{-31} \text{ J}$, $m = 27.5 \text{ pm}$, the particle behaves classically.

9.8 $E_0 = 3.92 \times 10^{-21} \text{ J}$.

9.9 $k = 260 \text{ N m}^{-1}$.

9.10 $\lambda = 13.2 \text{ }\mu\text{m}$.

9.11 $\lambda = 18.7 \text{ }\mu\text{m}$.

9.12 (a) $\Delta E = 2.2 \times 10^{-29} \text{ J}$; (b) $\Delta E = 3.14 \times 10^{-20} \text{ J}$.

9.14 $0, \pm 0.96\alpha$, or $\pm 2.02\alpha$.

9.15 $E_0 = 2.3421 \times 10^{-20} \text{ J}$.

9.17 Magnitude $= 2.58 \times 10^{-34} \text{ J s}$; possible projections $= 0, \pm 1.0546 \times 10^{-34} \text{ J s}$ and $\pm 2.1109 \times 10^{-34} \text{ J s}$.

Chapter 10

10.1 $I = 12.1 \text{ eV}$.

10.2 $r = 11.5a_0/Z$, $r = 3.53a_0/Z$, $r = 0$.

10.3 $r = 0$, $r = 1.382a_0$, $r = 3.618a_0$.

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

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

10.6 $P_{3s} = 4\pi r^2 \left(\frac{1}{4\pi}\right) \times \left(\frac{1}{243}\right) \times \left(\frac{Z}{a_0}\right)^3 \times (6 - 6\rho + \rho^2)^2 e^{-\rho}$,

$r = 0.74 a_0/Z$, $4.19 a_0/Z$ and $13.08 a_0/Z$.

10.7 $r = 1.76 a_0/Z$.

10.8 (a) angular momentum $= \frac{1}{2}\hbar = 2.45 \times 10^{-34} \text{ J s}$, angular nodes = 2, radial nodes = 1;

(b) angular momentum $= 2\frac{1}{2}\hbar = 1.49 \times 10^{-34} \text{ J s}$, angular nodes = 1, radial nodes = 0;

(c) angular momentum $= 2\frac{1}{2}\hbar = 1.49 \times 10^{-34} \text{ J s}$, 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) $r = 110 \text{ pm}$, $r = 20.1 \text{ ppm}$; (b) $r = 86 \text{ pm}$, $r = 29.4 \text{ ppm}$.

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

10.15 (a) $[\text{Ar}]3d^3$; (b) For $S = \frac{3}{2}$, $M_s = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$, for $S = \frac{1}{2}$, $M_s = \pm\frac{1}{2}$.

10.16 (a) $S = 2, 1, 0$; multiplicities = 5, 3, 1, respectively. (b) $S' = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$; multiplicities = 6, 4, 2 respectively.

10.17 $^1\text{F}_3$; $^3\text{F}_4$; $^3\text{F}_3$; $^3\text{F}_2$; $^1\text{D}_2$; $^3\text{D}_3$; $^3\text{D}_2$; $^3\text{D}_1$; $^1\text{P}_1$; $^3\text{P}_2$; $^3\text{P}_1$; $^3\text{P}_0$, the $^3\text{F}_2$ set of terms are the lower in energy.

10.18 (a) $J = 3, 2$ and 1, with 7, 5 and 3 states respectively;

(b) $J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, with 8, 6, 4 and 2 states respectively;

(c) $J = \frac{9}{2}, \frac{7}{2}$, with 10 and 8 states respectively.

10.19 (a) $^2\text{D}_{5/2}$ and $^2\text{D}_{3/2}$ (b) $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$.

Chapter 11

11.1 (a) $1\sigma^2 2\sigma^{*1}$; (b) $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$; (c) $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$.

11.2 (a) $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$; (b) $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$;
(c) $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}$.

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

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

11.8 Not appropriate.

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

11.10 $3.39 \times 10^{-16} \text{ J}$.

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 ($= \text{S}_1$), T_h has a centre of inversion ($= \text{S}_2$).

12.8 (a) $\text{C}_{\infty\text{v}}$; (b) D_3 ; (c) $\text{C}_{4\text{v}}$, $\text{C}_{2\text{v}}$; (d) C_s .

12.9 (a) $\text{D}_{2\text{h}}$; (b) $\text{D}_{2\text{h}}$; (c) (i) $\text{C}_{2\text{v}}$; (ii) $\text{C}_{2\text{v}}$; (iii) $\text{D}_{2\text{h}}$.

12.10 (a) $\text{C}_{\infty\text{v}}$; (b) $\text{D}_{5\text{h}}$; (c) $\text{C}_{2\text{v}}$; (d) $\text{D}_{3\text{h}}$; (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) $\text{B}_{3\text{U}}$ (x -polarized), $\text{B}_{2\text{U}}$ (y -polarized), $\text{B}_{1\text{U}}$ (z -polarized); (b) $\text{A}_{1\text{U}}$ or $\text{E}_{1\text{U}}$.

12.15 Yes, it is zero.

Chapter 13

13.1 (a) $7.73 \times 10^{-32} \text{ J m}^{-3} \text{ s}$; (b) $\nu = 6.2 \times 10^{-28} \text{ J m}^{-3} \text{ s}$.

13.2 $s = 6.36 \times 10^7 \text{ m s}^{-1}$.

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

- 13.4 (a) 160 MHz; (b) 16 MHz.
 13.5 $v = 3.4754 \times 10^{11} \text{ s}^{-1}$.
 13.6 (a) $I = 3.307 \times 10^{-47} \text{ kg m}^2$; (b) $R = 141 \text{ pm}$.
 13.7 (a) $I = 5.420 \times 10^{-46} \text{ kg m}^2$; (b) $R = 162.8 \text{ pm}$.
 13.8 $R = 116.21 \text{ pm}$.
 13.9 $R_{\text{CO}} = 116.1 \text{ pm}$; $R_{\text{CS}} = 155.9 \text{ pm}$.
 13.10 $\bar{\nu}_{\text{Stokes}} = 20\,603 \text{ cm}^{-1}$.
 13.11 $R = 141.78 \text{ pm}$.
 13.12 (a) H_2O , $\text{C}_{2\nu}$; (b) H_2O_2 , C_2 ; (c) NH_3 , $\text{C}_{3\nu}$; (d) N_2O , $\text{C}_{\infty\nu}$.
 13.13 (a) CH_2Cl_2 ; (b) CH_3CH_3 ; (d) N_2O .
 13.14 $k = 0.71 \text{ N m}^{-1}$.
 13.15 28.4 per cent.
 13.16 $k = 245.9 \text{ N m}^{-1}$.
 13.17 (a) 0.212; (b) 0.561.
 13.18 DF: $\bar{\nu} = 3002.3 \text{ cm}^{-1}$, DCl: $\bar{\nu} = 2143.7 \text{ cm}^{-1}$, DBr: $\bar{\nu} = 1885.8 \text{ cm}^{-1}$, DI: $\bar{\nu} = 1640.1 \text{ cm}^{-1}$.
 13.19 $\bar{\nu} = 2374.05 \text{ cm}^{-1}$, $x_c = 6.087 \times 10^{-3}$.
 13.20 $D_0 = 3.235 \times 10^4 \text{ cm}^{-1} = 4.01 \text{ eV}$.
 13.21 $\bar{\nu}_R = 2347.16 \text{ cm}^{-1}$.
 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 $\epsilon = 7.9 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$.
 14.4 $1.33 \times 10^{-3} \text{ mol dm}^{-3}$.
 14.5 $A = 1.56 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$.
 14.6 Rise.
 14.7 $\epsilon = 522 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.
 14.8 $\epsilon = 128 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $T = 0.13$.
 14.9 (a) 0.010 cm; (b) 0.033 cm.
 14.10 (a) $1.39 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$; (b) $1.39 \times 10^9 \text{ m mol}^{-1}$.
 14.11 Stronger.

Chapter 15

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

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 v . (b) $\frac{v - \nu^o(800 \text{ MHz})}{v - \nu^o(60 \text{ MHz})} = 13$.

- 15.9 (a) $4.2 \times 10^{-6} \text{ T}$; (b) $3.63 \times 10^{-5} \text{ T}$. Spectrum appears narrower at 650 MHz.
 15.11 $2.9 \times 10^3 \text{ s}^{-1}$.
 15.14 (a) The H and F nuclei are both chemically and magnetically equivalent. (b) The P and H nuclei chemically and magnetically equivalent in both the *cis*- and *trans*-forms.
 15.15 $B_1 = 9.40 \times 10^{-4} \text{ T}$, 6.25 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 $\pm 1.445 \pm 1.435 \pm 1.055 \text{ mT}$ from the centre, namely: 328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625 and 336.735 mT.
 15.21 (a) 332.3 mT; (b) 1209 mT.
 15.22 $I = 1$.

Chapter 16

- 16.1 $T = 623 \text{ K}$.
 16.2 (a) 15.9 pm, 5.04 pm; (b) 2.47×10^{26} , 7.82×10^{27} .
 16.3 $\frac{q_{\text{Xe}}}{q_{\text{He}}} = 187.9$.
 16.4 $q = 4.006$.
 16.5 $E = 7.605 \text{ kJ mol}^{-1}$.
 16.6 213 K.
 16.7 (a) 0.997, 0.994; (b) 0.999 99, 0.999 98.
 16.8 (a) (i) $\frac{n_2}{n_1} = 1.39 \times 10^{-11}$, $\frac{n_3}{n_1} = 1.93 \times 10^{-22}$;
 (ii) $\frac{n_2}{n_1} = 0.368$, $\frac{n_3}{n_1} = 0.135$;
 (iii) $\frac{n_2}{n_1} = 0.779$, $\frac{n_3}{n_1} = 0.607$;
 (b) $q = 1.503$; (c) $U_m = 88.3 \text{ J mol}^{-1}$;
 (d) $C_v = 3.53 \text{ J K}^{-1} \text{ mol}^{-1}$; (e) $S_m = 6.92 \text{ J K}^{-1} \text{ mol}^{-1}$.
 16.9 7.26 K.
 16.10 (a) $147 \text{ J K}^{-1} \text{ mol}^{-1}$; (b) $169.6 \text{ J K}^{-1} \text{ mol}^{-1}$.
 16.11 $10.7 \text{ J K}^{-1} \text{ mol}^{-1}$.
 16.12 (a)

Chapter 17

- 17.1 (a) $\text{O}_3 : 3R$ [experimental = 3.7R]
 (b) $\text{C}_2\text{H}_6 : 4R$ [experimental = 6.3R]
 (c) $\text{CO}_2 : \frac{5}{2}R$ [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 $q^K = 5837$, $\theta_R = 0.8479 \text{ K}$, $T = 0.3335 \text{ K}$.
 17.6 $S_m^R = 84.57 \text{ J K}^{-1} \text{ mol}^{-1}$.
 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, $S_m = 5.88 \text{ J mol}^{-1} \text{ K}^{-1}$.
 (b) At 500 K, $S_m = 16.48 \text{ J mol}^{-1} \text{ K}^{-1}$.
 17.10 $G_m^R - G_m^V(0) = -20.1 \text{ kJ mol}^{-1}$, $G_m^V - G_m^V(0) = -0.110 \text{ kJ mol}^{-1}$.
 17.11 $-3.65 \text{ kJ mol}^{-1}$.
 17.12 $S_m = 14.9 \text{ J mol}^{-1} \text{ K}^{-1}$.
 17.14 $K = 0.25$.

Chapter 18

- 18.1 SF_4 .
 18.2 $\mu = 1.4 \text{ D}$.
 18.3 $\mu = 9.45 \times 10^{-29} \text{ C m}$, $\theta = 194.0^\circ$.
 18.4 $\mu = 3.23 \times 10^{-30} \text{ C m}$, $\alpha = 2.55 \times 10^{-39} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$.
 18.5 $\varepsilon_r = 8.97$.
 18.6 $\mu^* = 3.71 \times 10^{-36} \text{ C m}$.
 18.7 $\alpha = 3.40 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$.
 18.8 $n_r = 1.10$.
 18.9 $\varepsilon_r = 16$.
 18.10 $p = 5.92 \text{ kPa}$.
 18.11 $\gamma = 7.12 \times 10^{-2} \text{ N m}^{-1}$.
 18.12 $p_{\text{in}} - p_{\text{out}} = 2.04 \times 10^5 \text{ Pa}$.

Chapter 19

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

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 $d_{121} = 214 \text{ pm}$, $d_{221} = 174 \text{ pm}$, $d_{244} = 87.2 \text{ pm}$.
 20.4 $\lambda = 86.7 \text{ pm}$.

20.5	hkl	$\sin \theta$	$\theta/^\circ$	$2\theta/^\circ$
	111	0.327	19.1	38.2
	200	0.378	22.2	44.4
	220	0.535	32.3	64.6

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

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

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

- 20.14 $\frac{2}{3}$.
 20.15 $\frac{r}{R} = 0.732$.
 20.16 (a) 57 pm; (b) 111 pm.
 20.17 $\frac{2V_{\text{atom}}}{V_{\text{cell}}} = 0.370$.
 20.18 contraction.
 20.20 $\lambda = 252 \text{ pm}$.
 20.21 $\Delta_L H^\circ(\text{MgBr}_2, \text{s}) = 2421 \text{ kJ mol}^{-1}$.
 20.23 strain $= 5.8 \times 10^{-2}$.
 20.24 $\Delta V = 0.003 \text{ dm}^3$.
 20.25 p-type.
 20.26 $2.71 \times 10^4 \text{ H}$.
 20.27 5.
 20.28 $-8.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$.
 20.29 $\chi_m = 1.58 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$, dimerization occurs.
 20.30 2.52 = effective unpaired spins, theoretical number = 2.
 20.31 $\chi_m = 1.85 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$.
 20.32 $r = 0.935$.

Chapter 21

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

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

Chapter 22

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

Chapter 23

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

Chapter 24

- 24.1** $z = 6.64 \times 10^9 \text{ s}^{-1}$, $Z_{AA} = 8.07 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}$, 1.6 per cent.
24.2 (a) (i) 2.4×10^{-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 $k = 1.7 \times 10^{-12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
24.5 $k_d = 3.2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ or $3.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
24.6 (a) $k_d = 1.97 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$; (b) $k_d = 2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
24.7 $k_d = 1.10 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ or $1.10 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,
 $t_{1/2} = 5.05 \times 10^{-8} \text{ s}$.

- 24.8** $P = 1.41 \times 10^{-3}$.
24.9 $v = 1.54 \times 10^8 \text{ mol dm}^{-3} \text{ s}^{-1}$.
24.10 $\Delta^\ddagger H = 48.52 \text{ kJ mol}^{-1}$, $\Delta^\ddagger S = -32.2 \text{ J K}^{-1} \text{ mol}^{-1}$.
24.11 $\Delta^\ddagger G = 46.8 \text{ kJ mol}^{-1}$.
24.12 $\Delta^\ddagger S = -93 \text{ J K}^{-1} \text{ mol}^{-1}$.
24.13 $\Delta^\ddagger S = -80.0 \text{ J K}^{-1} \text{ mol}^{-1}$.
24.14 (a) $\Delta^\ddagger S = -24.1 \text{ J K}^{-1} \text{ mol}^{-1}$; (b) $\Delta^\ddagger H = 27.5 \text{ kJ mol}^{-1}$;
 (c) $\Delta^\ddagger G = 34.7 \text{ kJ mol}^{-1}$.
24.15 $k_2^\circ = 1.08 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$.
24.16 $\lambda = 1.531 \text{ eV}$, $\langle H_{DA} \rangle = 9.39 \times 10^{-24} \text{ J}$.
24.17 $k_{\text{et}} = 1.4 \times 10^3 \text{ s}^{-1}$.

Chapter 25

- 25.1** (a) (i) $2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$, (ii) $5.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$;
 (b) (i) $3.81 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$, (ii) $7.60 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$.
25.2 $p = 7.3 \times 10^2 \text{ Pa}$.
25.3 $6.6 \times 10^4 \text{ s}^{-1}$.
25.4 $A = 18.8 \text{ m}^2$.
25.5 $V_{\text{mon}} = 9.7 \text{ cm}^3$.
25.6 $t_{1/2} = 200 \text{ s}$.
25.7 $E_d = 3.7 \times 10^3 \text{ J mol}^{-1}$.
25.8 (a) 0.32 kPa; (b) 3.9 kPa.
25.9 $\theta_1 = 0.75$, $\theta_2 = 0.25$.
25.10 (a) At 400 K: $4.9 \times 10^{-11} \text{ s}$, At 800 K: $2.4 \times 10^{-12} \text{ s}$;
 (b) At 400 K: $1.6 \times 10^{13} \text{ s}$, At 800 K: 1.4 s.
25.11 $p_2 = 6.50 \text{ kPa}$.
25.12 (a) $\theta = \frac{Kp}{1 + Kp}$; (b) $\theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$;
 (c) $\theta = \frac{(Kp)^{1/3}}{1 + (Kp)^{1/3}}$. 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 $\Delta_{\text{ad}} H^\circ = -6.40 \text{ kJ mol}^{-1}$.
25.14 $E_d = 2.85 \times 10^5 \text{ J mol}^{-1}$. (a) $t = 1.48 \times 10^{36} \text{ s}$; (b) $t = 1.38 \times 10^{-4} \text{ s}$.
25.15 $\varepsilon = 2.8 \times 10^8 \text{ V m}^{-1}$.
25.16 167 mV.
25.17 $j_0 = 1.6 \text{ mA cm}^{-2}$.
25.18 $j_2 = 8.5 \text{ mA cm}^{-2}$.
25.19 (a) $j = 0.34 \text{ A cm}^{-2}$;
 (b) $j = 0.34 \text{ A cm}^{-2}$. The validity of the Tafel equation improves as the overpotential increases.
25.20 $j_{\text{lim}} = 1.3 \text{ A m}^{-2}$.
25.21 $[\text{Fe}^{2+}] = 4 \times 10^{-6} \text{ mol dm}^{-3}$.
25.22 $j = (2.5 \text{ mA cm}^{-2}) \times [(e^{(0.42)E'/f}) \times (3.41 \times 10^{-6}) - e^{(-0.58)E'/f} \times (3.55 \times 10^7)]$.
25.23 At $r = 0.1$: $j/j_0 = 1.5 \text{ A cm}^{-2}$,
 At $r = 1$: $j/j_0 = 4.8 \text{ A cm}^{-2}$,
 At $r = 10$: $j/j_0 = 15 \text{ A cm}^{-2}$.
25.24 0.61 V.
25.25 For the Cu, $\text{H}_2|\text{H}^+$ electrode: $N = 6.2 \times 10^{12} \text{ s}^{-1} \text{ cm}^{-2}$, $f = 4.2 \times 10^{-3} \text{ s}^{-1}$.
 For the Pt|Ce⁴⁺, Ce³⁺ electrode: $N = 2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}$, $f = 0.17 \text{ s}^{-1}$.
25.26 (a) 5.1 GΩ; (b) 10 GΩ.
25.29 Deposition would not occur.
25.30 Iron can be deposited.
25.31 $E^\circ = 1.80 \text{ V}$, $P = 0.180 \text{ W}$.
25.32 3.0 mm y^{-1} .

Solutions to odd problems

Chapter 1

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

Chapter 2

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

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

Chapter 3

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

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

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

$$f = 0.9991 \text{ atm}$$

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

$$3.39 \quad 13 \text{ per cent increase.}$$

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

$$\varepsilon = 0.47$$

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

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

$$3.45 \quad (a) 1.00 \text{ kJ}; (b) 8.4 \text{ kJ.}$$

Chapter 4

$$4.1 \quad 196.0 \text{ K}, 11.1 \text{ Torr.}$$

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

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

$$4.7 \quad 22^\circ\text{C.}$$

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

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

$$4.15 \quad 9.8 \text{ Torr.}$$

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

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

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

Chapter 5

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

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

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

$$5.7 \quad 4 \text{ ions.}$$

$$5.11 \quad (a) \text{ propionic acid: } V_1 = V_{m,1} + a_0 x_2^2 + a_1 (3x_1 - x_2)x_2^2, \\ \text{oxane: } V_2 = V_{m,2} + a_0 x_1^2 + a_1 (x_1 - 3x_2)x_1^2,$$

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

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

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

$$5.17 \quad \mu_A = \mu_A^* + RT \ln x_A + gRT x_B^2$$

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

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

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

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

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

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

Chapter 6

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

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

$$6.7 \quad \text{MgCu}_2: 16 \text{ per cent mg by mass, Mg}_2\text{Cu: 43 per cent mg by mass.}$$

$$6.9 \quad (a) \text{ Eutectic: } 40.2 \text{ at per cent Si at } 1268^\circ\text{C}; 69.4 \text{ at per cent Si at } 1030^\circ\text{C. Congruent melting compounds: Ca}_2\text{Si} = 1314^\circ\text{C; CaSi} = 1324^\circ\text{C. Incongruent melting compounds: CaSi}_2 = 1040^\circ\text{C;}$$

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

$$(c) (i) n_{\text{Si}}/n_{\text{liq}} = 0.53 \text{ at slightly above } 1030^\circ\text{C, (ii) } n_{\text{Si}}/n_{\text{CaSi}_2} = 0.665 \text{ slightly below } 1030^\circ\text{C.}$$

$$6.13 \quad (i) \text{ Below a denaturant concentration of } 0.1 \text{ only the native and unfolded forms are stable.}$$

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

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

Chapter 7

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

$$7.3 \quad \Delta_r H^\circ = 8.48 R.$$

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

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

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

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

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

$$7.15 \quad \text{pH} = 2.0.$$

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

$$7.19 \quad \gamma = 0.533.$$

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

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

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

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

$$7.23 \quad -1.15 \text{ V.}$$

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

$$7.31 \quad \text{Yes.}$$

$$7.33 \quad (b) +0.206 \text{ V.}$$

$$7.35 \quad (\text{iv}) \text{ HNO}_3 \cdot 3\text{H}_2\text{O} \text{ is most stable.}$$

Chapter 8

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

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

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

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

$$8.15 \quad (a) \text{ Yes, eigenvalue} = ik; (b) \text{ No}; (c) \text{ Yes, eigenvalue} = 0; (d) \text{ No}; (e) \text{ No.}$$

$$8.17 \quad (a) \text{ Yes, eigenvalue} = -k^2;$$

$$(b) \text{ Yes, eigenvalue} = -k^2;$$

$$(c) \text{ Yes, eigenvalue} = 0;$$

$$(d) \text{ Yes, eigenvalue} = 0;$$

$$(e) \text{ No.}$$

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

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

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

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

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

$$8.29 \quad (a) \text{Methane is unstable above } 825 \text{ K}; (b) \lambda_{\text{max}} (1000 \text{ K}) = 2880 \text{ nm};$$

$$(c) \text{Excitance ratio} = 7.7 \times 10^{-4}; \text{Energy density ratio} = 8.8 \times 10^{-3};$$

$$(d) 2.31 \times 10^{-7}, \text{ it hardly shines.}$$

Chapter 9

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

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

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

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

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

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

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

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

$$9.23 \quad (a) E = 0, \text{ angular momentum} = 0; (b) E = \frac{3\hbar^2}{I}, \text{ angular}$$

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

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

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

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

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

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

Chapter 10

$$10.1 \quad n_2 \rightarrow 6, \text{ transitions occur at } 12\,372 \text{ nm}, 7503 \text{ nm}, 5908 \text{ nm}, 5129 \text{ nm},$$

$$\dots, 3908 \text{ nm (at } n_2 = 15), \text{ converging to } 3282 \text{ nm as } n_2 \rightarrow \infty.$$

$$10.3 \quad R_{\text{Li}^{2+}} = 987\,663 \text{ cm}^{-1}, \text{ the Balmer transitions lie at } \tilde{\nu} = 137\,175 \text{ cm}^{-1},$$

$$85\,187 \text{ cm}^{-1}, 122.5 \text{ eV}.$$

$$10.5 \quad {}^2P_{1/2} \text{ and } {}^2P_{3/2}, \text{ of which the former has the lower energy, } {}^2P_{3/2} \text{ and}$$

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

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

$$10.9 \quad (a) \Delta \tilde{\nu} = 0.9 \text{ cm}^{-1}, (b) \text{Normal Zeeman splitting is small compared to}$$

$$\text{the difference in energy of the states involved in the transition.}$$

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

$$10.13 \quad (b) \text{For } 3s, \rho_{\text{node}} = 3 + \sqrt{3} \text{ and } \rho_{\text{node}} = 3 - \sqrt{3}, \text{ no nodal plane; for } 3p_x,$$

$$\rho_{\text{node}} = 0 \text{ and } \rho_{\text{node}} = 4, yz \text{ nodal plane } (\phi = 90^\circ); \text{ for } 3d_{xy}, \rho_{\text{node}} = 0,$$

$$xz \text{ nodal plane } (\phi = 0) \text{ and } yz \text{ nodal plane } (\phi = 90^\circ); (c) (r)_{3s} = \frac{27a_0}{2}.$$

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

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

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

$$329\,170 \text{ cm}^{-1}, {}^3\text{He} = 329\,155 \text{ cm}^{-1}.$$

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

Chapter 11

$$11.3 \quad R = 2.1a_0.$$

$$11.7 \quad (a) P = 8.6 \times 10^{-7} / P = 2.0 \times 10^{-6};$$

$$(b) P = 8.6 \times 10^{-7} / P = 2.0 \times 10^{-6};$$

$$(c) P = 3.7 \times 10^{-7} / P = 0;$$

$$(d) P = 4.9 \times 10^{-7} / P = 5.5 \times 10^{-7}.$$

$$11.13 \quad \text{Delocalization energy} = 2\{E_{\text{with resonance}} - E_{\text{without resonance}}\}$$

$$= \{(\alpha_O - \alpha_N)^2 + 12\beta^2\}^{1/2} - \{(\alpha_O - \alpha_N)^2 + 4\beta^2\}^{1/2}$$

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

$$(b) 8.913 \text{ eV}.$$

$$11.29 \quad (a) \text{linear relationship}; (b) E^* = -0.122 \text{ V}; (c) E^* = -0.174 \text{ V,}$$

$$\text{ubiquinone a better oxidizing agent than plastoquinone.}$$

Chapter 12

$$12.1 \quad (a) D_{3d}; (b) \text{chair: } D_{3d}, \text{boat: } C_{2v}; (c) D_{2h}; (d) D_3; (e) D_{4d}; (i) \text{Polar:}$$

$$\text{Boat } C_6\text{H}_{12}; (ii) \text{Chiral: } [\text{Co(en)}_3]^{3+}.$$

$$12.3 \quad C_2\sigma_h = i.$$

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

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.

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

$$\text{may participate in bonding.}$$

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

$$12.13 \quad (a) C_{2v}, f \rightarrow 2A_1 + A_2 + 2B_1 + 2B_2;$$

$$(b) C_{3v}, f \rightarrow A_2 + 3E;$$

$$(c) T_d, f \rightarrow A_1 + T_1 + T_2;$$

$$(d) O_h, f \rightarrow A_{2U} + T_{1U} + T_{2U}.$$

Lanthanide ion (a) tetrahedral complex: $f \rightarrow A_1 + T_1 + T_2$ in T_d symmetry, and there is one nondegenerate orbital and two sets of triply degenerate orbitals. (b) octahedral complex: $f \rightarrow A_{2U} + T_{1U} + T_{2U}$, and the pattern of splitting is the same.

$$12.15 \quad \text{irreducible representations: } 4A_1 + 2B_1 + 3B_2 + A_2$$

Chapter 13

13.1	T/K	$E/J \text{ m}^{-3}$	$E_{\text{class}}/J \text{ m}^{-3}$
(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** $I = 2.728 \times 10^{-47}$ kg m², $R = 129.5$ 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) $\bar{\nu} = 152$ m⁻¹, $k = 2.72 \times 10^{-4}$ kg s⁻², $I = 2.93 \times 10^{-46}$ kg m², $B = 95.5$ m⁻¹.
(b) $x_c = 0.96$.
- 13.19** (a) C_{3v}; (b) 9; (c) 2A₁ + A₂ + 3E. (d) All but the A₂ mode are infrared active. (e) All but the A₂ 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** HgCl₂: 230, HgBr₂: 240, HgI₂: 250 pm.
- 13.27** (a) infrared active; (b) 796 cm⁻¹; (c) O₂: 2, O₂⁻: 1.5, O₂²⁻: 1; (d) Fe₂³⁺O₂²⁻; (e) Structures 6 and 7 are consistent with this observation, but structures 4 and 5 are not.
- 13.29** $s = 0.0768$ c, $T = 8.34 \times 10^5$ K.
- 13.31** $B = 2.031$ cm⁻¹; $T = 2.35$ K.

Chapter 14

- 14.1** 49 364 cm⁻¹.
- 14.3** 14 874 cm⁻¹.
- 14.5** $\mathcal{A} = 1.1 \times 10^6$ dm³ mol⁻¹ cm⁻², Excitations from A₁ to A₁, B₁, and B₂ terms are allowed.
- 14.7** 5.06 eV.

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

- 14.11** (a) $\frac{n}{V} = 1.7 \times 10^{-9}$ mol dm⁻³, (b) $N = 6.0 \times 10^2$.
- 14.15** The transition moves toward the red as the chain lengthens and the apparent color of the dye shifts towards blue.
- 14.21** (a) 3 + 1, 3 + 3; (b) 4 + 4, 2 + 2.
- 14.23** 4.4×10^3 .
- 14.25** $\mathcal{A} = 1.24 \times 10^5$ dm³ mol⁻¹ dm⁻².
- 14.27** (a) $\mathcal{A} = 2.24 \times 10^5$ dm³ mol⁻¹ cm⁻²; (b) $A = 0.185$;
(c) $\varepsilon = 135$ dm³ mol⁻¹ cm⁻¹.
- 14.29** $V_1 - V_0 = 3.1938$ eV, $\bar{\nu}_1 - \bar{\nu}_0 = 79.538$ cm⁻¹, $\bar{\nu}_0 = 2034.3$ cm⁻¹, $T_{\text{eff}} = 1321$ K.

Chapter 15

- 15.1** $B_0 = 10.3$ T, $\frac{\delta N}{N} \approx 2.42 \times 10^{-5}$, β state lies lower.
- 15.3** 300×10^{-6} Hz \pm 10 Hz, 0.29 s.

- 15.5** Both fit the data equally well.
- 15.9** Width of the CH₃ spectrum is $3a_{\text{H}} = 6.9$ mT. The width of the CD₃ spectrum is $6a_{\text{D}}$. The overall width is $6a_{\text{D}} = 2.1$ mT.
- 15.11** $P(\text{N}2s) = 0.10$, $P(\text{N}2p_z) = 0.38$, total probability: $P(\text{N}) = 0.48$, $P(\text{O}) = 0.52$, hybridization ratio = 3.8, $\Phi = 131^\circ$.
- 15.13** $\sigma_d = \frac{e^2 \mu_0 Z}{12 \pi m_e a_0} = 1.78 \times 10^{-5} Z$.
- 15.15** $R = 158$ pm.
- 15.17** $I(\omega) \approx \frac{1}{2} \frac{A \tau}{1 + (\omega_0 - \omega)^2 \tau^2}$.
- 15.21** $\frac{-g_I \mu_N \mu_O m_I}{4 \pi R^3} (\cos^2 \theta_{\max} + \cos \theta_{\max}), \langle \mathcal{B}_{\text{nucl}} \rangle = 0.58$ mT.

Chapter 16

- 16.1** $W = 2 \times 10^{40}$, $S = 1.282 \times 10^{-21}$ J K⁻¹, $S_1 = 0.637 \times 10^{-21}$ J K⁻¹, $S_2 = 0.645 \times 10^{-21}$ J K⁻¹.
- 16.3** $\frac{\Delta W}{W} \approx 2.4 \times 10^{25}$.
- 16.5** $T = 3.5 \times 10^{-15}$ K, $q = 7.41$.
- 16.7** (a) (i) $q = 5.00$; (ii) $q = 6.26$;
(b) $p_0 = 1.00$ at 298 K, $p_0 = 0.80$ at 5000 K; $p_2 = 6.5 \times 10^{-11}$ at 298 K, $p_2 = 0.12$ at 5000 K.
(c) (i) $S_{\text{m}} = 13.38$ J K⁻¹ mol⁻¹, (ii) $S_{\text{m}} = 18.07$ 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, $S_{\text{m}} = 11.2$ J K⁻¹ mol⁻¹, At 500 K, $S_{\text{m}} = 11.4$ J K⁻¹ mol⁻¹.
- 16.11** (a) At 100 K: $q = 1.049$, $p_0 = 0.953$, $p_1 = 0.044$, $p_2 = 0.002$;
 $U_{\text{m}} - U_{\text{m}}(0) = 123$ J mol⁻¹, $S_{\text{m}} = 1.63$ J K⁻¹ mol⁻¹.
(b) At 298 K: $q = 1.55$, $p_0 = 0.645$, $p_1 = 0.230$, $p_2 = 0.083$,
 $U_{\text{m}} - U_{\text{m}}(0) = 1348$ J mol⁻¹, $S_{\text{m}} = 8.17$ 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** $C_{V,\text{m}} = 4.2$ J K⁻¹ mol⁻¹, $S_{\text{m}} = 15$ J K⁻¹ mol⁻¹.
- 17.5** $q = 19.90$.
- 17.7** $S_{\text{m}}^* = 199.4$ J mol⁻¹ K⁻¹.
- 17.11** At 298 K: $K = 3.89$. At 800 K: $K = 2.41$.
- 17.13** (a) $\theta_{\text{R}} = 87.55$ K, $\theta_{\text{V}} = 6330$ K.
- 17.16** (b) $J_{\max} = \left(\frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2}$; (c) $T \approx 374$ K.
- 17.17** (a) $q^{\text{R}} = 660.6$; (b) $q^{\text{R}} = 4.26 \times 10^4$.
- 17.23** $S = 9.57 \times 10^{-15}$ J K⁻¹.
- 17.25** $G_{\text{m}}^* - G_{\text{m}}^*(0) = 513.5$ kJ mol⁻¹.
- 17.27** At 10 K, $G_{\text{m}}^* - G_{\text{m}}^*(0) = 660.8$ J mol⁻¹.
At 1000 K, $G_{\text{m}}^* - G_{\text{m}}^*(0) = 241.5$ kJ mol⁻¹.

Chapter 18

- 18.1** (a) $\varepsilon = 1.1 \times 10^8$ V m⁻¹; (b) $\varepsilon = 4 \times 10^9$ V m⁻¹; (c) $\varepsilon = 4$ kV m⁻¹.
- 18.3** $\alpha' = 1.2 \times 10^{-23}$ cm³, $\mu = 0.86$ D.
- 18.5** $\alpha' = 2.24 \times 10^{-24}$ cm³, $\mu = 1.58$ D, $P'_{\text{m}} = 5.66$ cm³ mol⁻¹, $\mu = 1.58$ D.
- 18.7** (a) $\varepsilon = 1.51 \times 10^{-23}$ J, $R_{\text{c}} = 265$ pm.

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

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

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

Chapter 19

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

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

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

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

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

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

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

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

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

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

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

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

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

For BSV, $\frac{\Pi - \Pi^0}{\Pi^0} = 2.6 \times 10^{-2}$ corresponding to 2.6 per cent.

For Hb, $\frac{\Pi - \Pi^0}{\Pi^0} = 5.0 \times 10^{-2}$ corresponding to 5 per cent.

19.25 (a)

$\theta / ^\circ$	20	45	90
$I_{\text{rod}} / I_{\text{cc}}$	0.976	0.876	0.514

(b) 90° .

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

19.29 $\text{pH} = 3.85$.

Chapter 20

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

20.3 Yes, the data support.

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

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

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

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

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

20.17 0.736 eV .

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

20.21 $x = 0.41$.

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

For an orthorhombic cell, $V = abc$.

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

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

Chapter 21

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

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

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

21.9 $\Lambda_m^\circ = 12.6 \text{ mS m}^2 \text{ mol}^{-1}$; $\chi = 7.30 \text{ mS m}^2 \text{ mol}^{-1} \text{ M}^{-1/2}$.

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

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

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

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

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

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

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

(c) $4.1 \times 10^{-20} \text{ N molecule}^{-1}$.

21.17 9.3 kJ mol^{-1} .

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

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

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

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

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

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

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

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

Chapter 22

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

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

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

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

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

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

22.13 $\text{rate} = kK_1 K_2 [\text{HCl}]^3 [\text{CH}_3\text{CH}=\text{CH}_2]$; look for evidence of proposed intermediates, e.g. using infrared spectroscopy to search for $(\text{HCl})_2$.

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

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

22.19 The product concentration ratio increases.

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

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

22.29 2720 y .

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

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

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

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

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

Chapter 23

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

$$\frac{d[\text{SiH}_4]}{dt} = \left(\frac{k_1 k_4 k_5}{k_6} \right)^{1/2} [\text{N}_2\text{O}][\text{SiH}_4]^{1/2}$$

23.5 $\frac{d[\text{HI}]}{dt} = \frac{2k_b k_a [\text{I}_2][\text{H}_2]}{k'_a + k_b [\text{H}_2]}$. This simple rate law is observed when step (b) is rate-determining so that step (a) is a rapid equilibrium and $[\text{I}^-]$ is in an approximate steady state. This is equivalent to $k_b [\text{H}_2] = k'_a$ and hence, $\frac{d[\text{HI}]}{dt} = 2k_b K [\text{I}_2][\text{H}_2]$.

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

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

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

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

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

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

23.27 Uncompetitive.

23.29 $R = 2.6 \text{ nm}$.

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

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

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

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

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

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

for $\text{NO} + \text{O}_2 \rightarrow \text{O} + \text{NO}_2$, $E_{a,\text{eff}} = 253 \text{ kJ mol}^{-1}$, this value is consistent with the low range of the experimental values of $E_{a,\text{eff}}$.

Chapter 24

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

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

24.5 2-.

24.9 (a) $-\frac{d[\text{F}_2\text{O}]}{dt} = k_1 [\text{F}_2\text{O}]^2 + k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{F}_2\text{O}]^{3/2}$; (b) $\Delta H(\text{FO}-\text{F}) \approx$

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

24.11 Linear regression analysis of $\ln(\text{rate constant})$ against $1/T$ yields the following results: $R = 0.99976$ and $R = 0.99848$, which indicate that the data are a good fit.

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

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

24.23 For O_2 with ethyl: $P = 1.6 \times 10^{-3}$; For O_2 with cyclohexyl: $P = 1.8 \times 10^{-3}$.

24.25 $z_A = +3.0$.

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

Chapter 25

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

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

For the collision frequencies:

$Z/(\text{atom}^{-1} \text{ s}^{-1})$	Hydrogen		Propane	
	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) $c = 164$, $V_{\text{mon}} 13.1 \text{ cm}^3$; (b) $c = 264$, $V_{\text{mon}} 12.5 \text{ cm}^3$.

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

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

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

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

25.15 $\delta = 2.5 \times 10^{-4} \text{ m}$ 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. $V_{\text{mon}} = 75.4 \text{ cm}^3$, $c = 3.98$.

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

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

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

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

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

25.37 (a) Therefore, the metals with a thermodynamic tendency to corrode in moist conditions at $\text{pH} = 7$ 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 $0.28 \text{ mg cm}^{-2} \text{ d}^{-1}$.

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(T) denotes a table in the Data Section.

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