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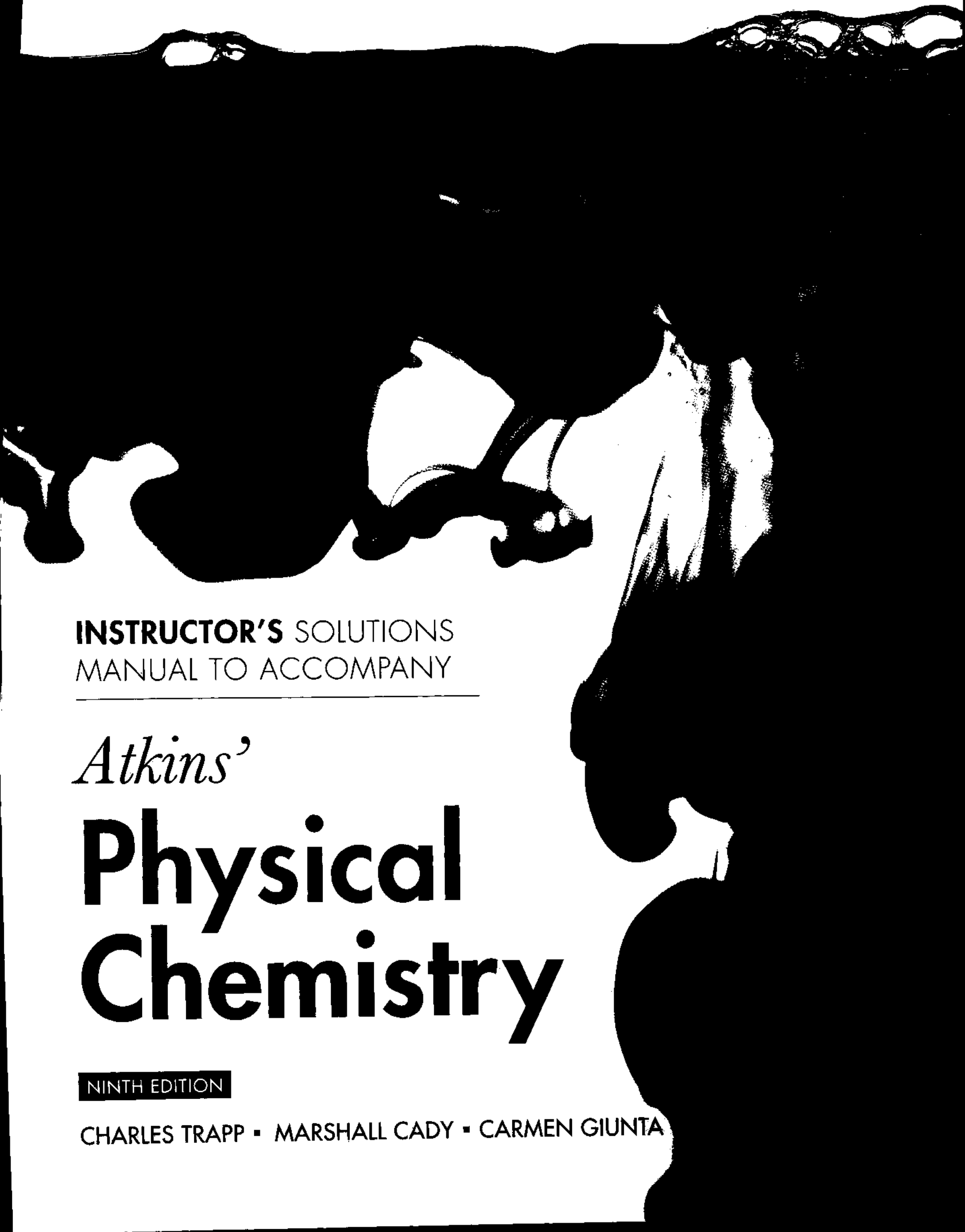

INSTRUCTOR'S SOLUTIONS
MANUAL TO ACCOMPANY

Atkins'
Physical Chemistry

NINTH EDITION

CHARLES TRAPP ▪ MARSHALL CADY ▪ CARMEN GIUNTA

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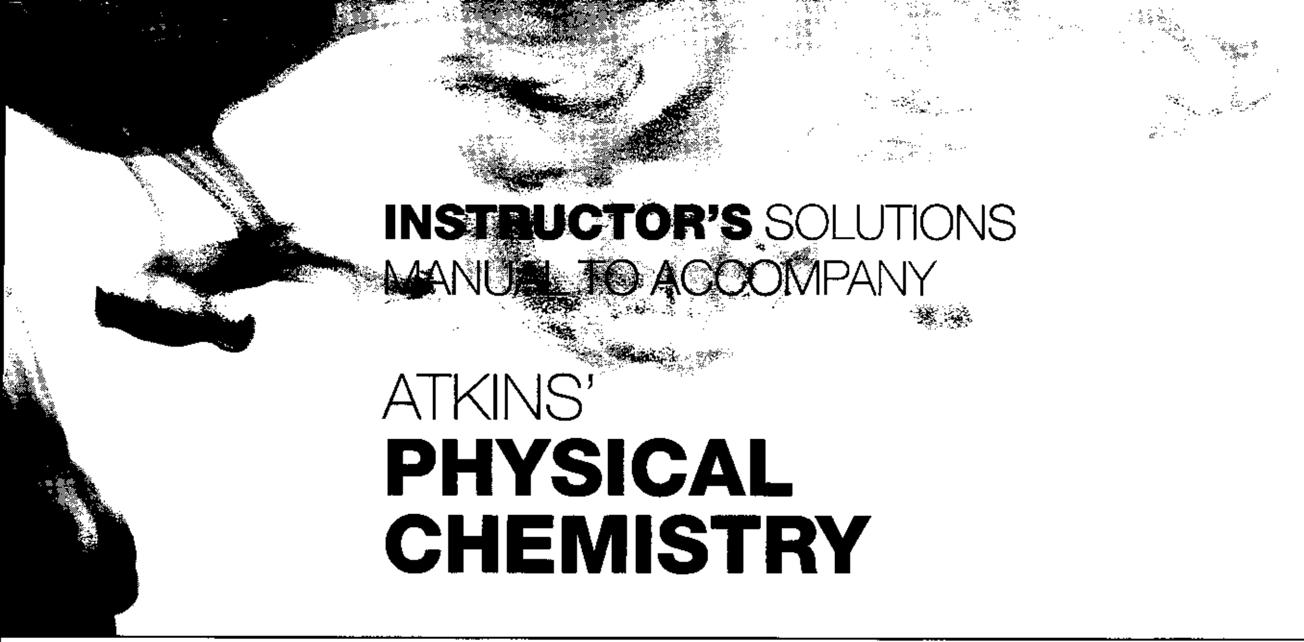
ATKINS'
PHYSICAL
CHEMISTRY



INSTRUCTOR'S SOLUTIONS MANUAL TO ACCOMPANY

ATKINS' PHYSICAL CHEMISTRY

Ninth Edition

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Preface

This manual provides detailed solutions to all the end-of-chapter (b) Exercises, and to the even-numbered Discussion Questions and Problems. Solutions to Exercises and Problems carried over from previous editions have been reworked, modified, or corrected when needed.

The solutions to some of the Exercises and many of the Problems in this edition relied more heavily on the mathematical, graphical, and molecular modelling software that is now generally accessible to physical chemistry students. This is particularly true for some of the new Problems that specifically request the use of such software for their solutions. We used the following software for many of the solutions in this manual: Excel™ for spreadsheet calculations and graphing, and Mathcad™ for mathematical calculations and the plotting of the results. When a quantum-chemical calculation or molecular modelling process has been called for, we have often provided the solution with PC Spartan Pro because of its common availability. However, the majority of the Exercises and many of the Problems can still be solved with a modern hand-held scientific calculator.

In general, we have adhered rigorously to the rules for significant figures in displaying the final answers. However, when intermediate answers are shown, they are often given with one more figure than would be justified by the data. These excess digits are indicated with an overline.

The solutions in this manual have been carefully cross-checked for errors not only by ourselves, but also very thoroughly by Valerie Walters, who made many helpful suggestions for improvement. We expect that most errors have been eliminated, but would be grateful to any readers who bring any remaining ones to our attention.

We warmly thank our publishers, especially Jonathan Crowe and Jessica Fiorilla, as well as Dave Quinn, for their patience in guiding this complex, detailed project to completion. We also thank Peter Atkins and Julio de Paula for the opportunity to participate in the development of their outstanding Physical Chemistry text.

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Fundamentals

Exercises

F.1 Atoms

F1.1(b) The **atomic number, Z**, is the number of protons in an atom. These protons are located within the nucleus.

The **nucleon number, A**, which is also commonly called the **mass number**, is the total number of protons and neutrons in an atom. These nucleons are located within the nucleus.

F1.2(b)

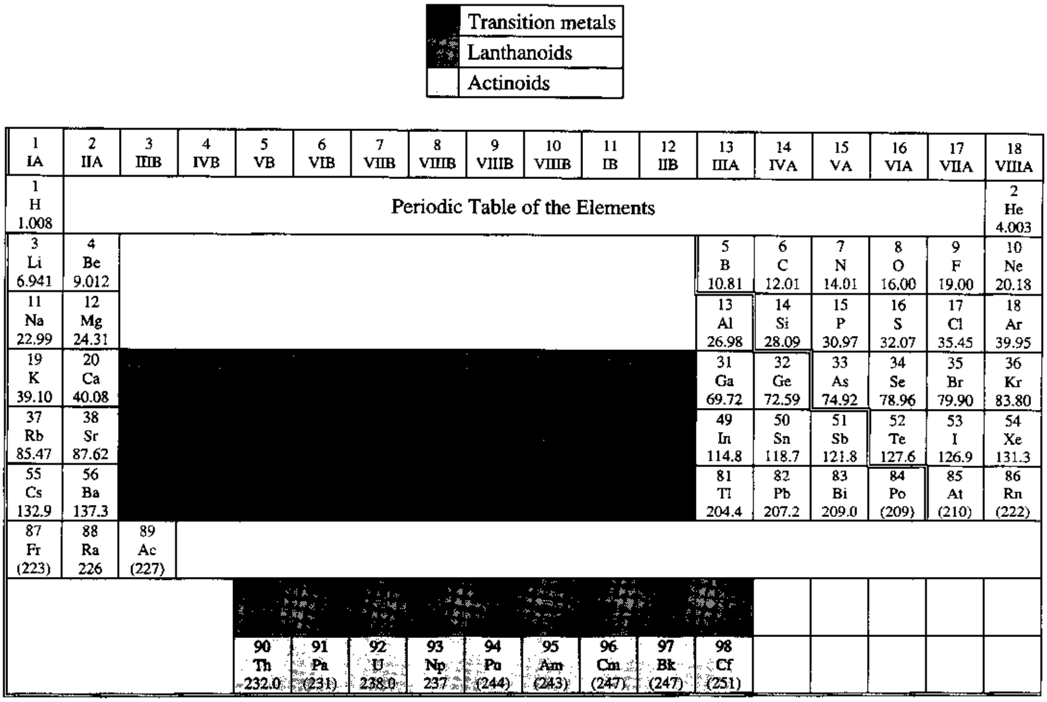
	Example	Element	Ground-state electronic configuration
(a)	Group 3	Sc, scandium	$[Ar]3d^1 4s^2$
(b)	Group 5	V, vanadium	$[Ar]3d^3 4s^2$
(c)	Group 13	Ga, gallium	$[Ar]3d^{10} 4s^2 4p^1$

F1.3(b) (a) Chemical formula and name: CaH_2, calcium hydride
Ions: Ca^{2+} and H^-
Oxidation numbers of the elements: calcium, +2; hydrogen, −1

(b) Chemical formula and name: CaC_2, calcium carbide
Ions: Ca^{2+} and C_2^{2-} (a polyatomic ion)
Oxidation numbers of the elements: calcium, +2; carbon, −1

(c) Chemical formula and name: LiN_3, lithium azide
Ions: Li^+ and N_3^- (a polyatomic ion)
Oxidation numbers of the elements: lithium, +1; nitrogen, $-\frac{1}{3}$

F1.4(b)

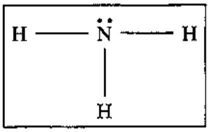


■	Transition metals
▨	Lanthanoids
☐	Actinoids

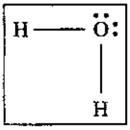
1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.008	Periodic Table of the Elements																2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	■	■	■	■	■	■	■	■	■	■	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	■	■	■	■	■	■	■	■	■	■	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	■	■	■	■	■	■	■	■	■	■	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac (227)															
				▨	▨	▨	▨	▨	▨	▨	▨	▨					
				90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np 237	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)					

F.2 Molecules

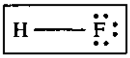
F2.1(b) (a) Ammonia, NH_3, illustrates a molecule with one lone pair on the central atom.

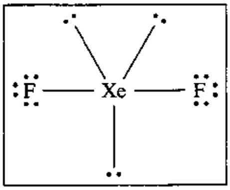


(b) Water, H_2O, illustrates a molecule with two lone pairs on the central atom.

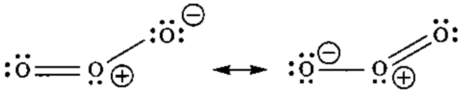


(c) The hydrogen fluoride molecule, HF, illustrates a molecule with three lone pairs on the central atom. Xenon difluoride has three lone pairs on both the central atom and the two peripheral atoms.

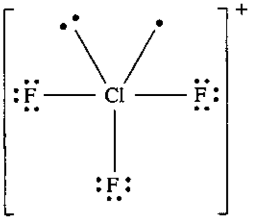




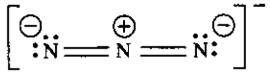
F2.2(b) (a) Ozone, O_3. Formal charges (shown in circles) may be indicated.



(b) ClF_3^+



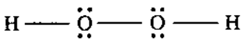
(c) azide anion, N_3^-



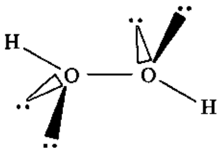
F2.3(b) The central atoms in XeF_4, PCl_5, SF_4, and SF_6 are hypervalent.

F2.4(b) Molecular and polyatomic ion shapes are predicted by drawing the Lewis structure and applying the concepts of VSEPR theory.

(a) H_2O_2
Lewis structure:

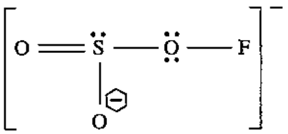


Orientations caused by repulsions between two lone pairs and two bonding pairs around each oxygen atom:

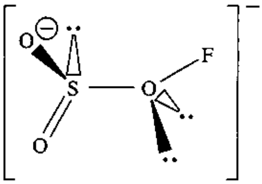


Molecular shape around each oxygen atom: bent (or angular) with bond angles somewhat smaller than 109.5°.

(b) FSO_3^-
Lewis structure:
(Formal charged is circled.)



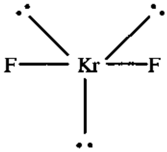
Orientations around the sulfur are caused by repulsions between one lone pair, one double bond, and two single bonds, while orientations around the oxygen to which fluorine is attached are caused by repulsions between two lone pairs and two single bonds:



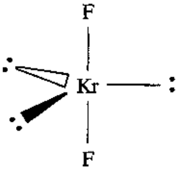
Molecular shape around the sulfur atom is trigonal pyramidal with bond angles somewhat smaller than 109.5° while the shape around the oxygen to which fluorine is attached is bent (or angular) with a bond angle somewhat smaller than 109.5°.

(c) KrF_2

Lewis structure:



Orientations caused by repulsions between three lone pairs and two bonding pairs:

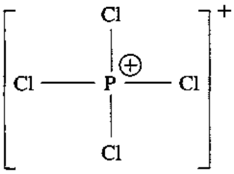


Molecular shape: linear with a 180° bond angle.

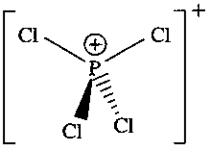
(d) PCl_4^+

Lewis structure:

(Formal charge is shown in a circle.)



Orientations caused by repulsions between four bonding pairs (no lone pair):



Molecular shape: tetrahedral and bond angles of 109.5°.

F2.5(b) (a) C——H Non-polar or weakly polar toward the slightly more electronegative carbon.

(b) $\overset{\delta^+}{\text{P}}$——$\overset{\delta^-}{\text{S}}$ (c) $\overset{\delta^+}{\text{N}}$——$\overset{\delta^-}{\text{Cl}}$

F2.6(b) (a) O_3 is a bent molecule that has a small dipole as indicated by consideration of electron densities and formal charge distributions.

(b) XeF_2 is a linear, non-polar molecule.
(c) NO_2 is bent, polar molecule.
(d) C_6H_{14} is a non-polar molecule.

F2.7(b) In the order of increasing dipole moment: $XeF_2 \sim C_6H_{14}$, NO_2, O_3

F.3 Bulk matter

F3.1(b) Condensed forms of matter (liquids and solids) have relatively high densities because of the close proximity of constituent elemental atoms or constituent molecules; compressibility is low and attractive forces are strong between neighbours. Perfect gases have low densities and they are highly compressible; intermolecular forces of attraction are negligibly small.

F3.2(b) (a) Pressure is an intensive property.
(b) Specific heat capacity is an intensive property.
(c) Weight is an extensive property.
(d) Molality is an intensive property.

F3.3(b) (a) $n = \dfrac{m}{M} = 5.0\text{ g}\left(\dfrac{1\text{ mol}}{180.16\text{ g}}\right) = \boxed{0.028\text{ mol}}$ [F.1]

(b) $N = nN_A = 0.028\text{ mol}\left(\dfrac{6.0221\times10^{23}\text{ molecules}}{\text{mol}}\right) = \boxed{1.7\times10^{22}\text{ molecules}}$

F3.4(b) (a) $(222\text{ atm})\times\left(\dfrac{101325\text{ Pa}}{1\text{ atm}}\right) = \boxed{2.25\times10^{7}\text{ Pa}}$

(b) Since 1 bar = 10^5 Pa, the above pressure is $\boxed{225\text{ bar}}$.

F3.5(b) $\theta/°\text{C} = T/\text{K} - 273.15 = 90.18 - 273.15 = -182.97$ [F.2]

$\boxed{\theta = -182.97\text{ °C}}$

F3.6(b) The absolute zero of temperature is 0 K and 0 °R. Using the scaling relationship 1 °F/1 °R (given in the exercise) and knowing the scaling ratios 5 °C/9 °F (see Exercise F3.6a) and 1 K/1 °C, we find the scaling factor between the Kelvin scale and the Rankine scale to be:

$$\left(\frac{1\text{ °F}}{1\text{ °R}}\right)\times\left(\frac{5\text{ °C}}{9\text{ °F}}\right)\times\left(\frac{1\text{ K}}{1\text{ °C}}\right) = \frac{5\text{ K}}{9\text{ °R}}$$

The zero values of the absolute zero of temperature on both the Kelvin and Rankine scales and the value of the scaling relationship implies that:

$$\boxed{T/\mathrm{K} = \tfrac{5}{9} \times (\theta_\mathrm{R}/{}^\circ\mathrm{R}) \quad \text{or} \quad \theta_\mathrm{R}/{}^\circ\mathrm{R} = \tfrac{9}{5} \times (T/\mathrm{K})}$$

Normal freezing point of water:

$$\theta_\mathrm{R}/{}^\circ\mathrm{R} = \tfrac{9}{5} \times (T/\mathrm{K}) = \tfrac{9}{5} \times (273.15) = 491.67$$

$$\theta_\mathrm{R} = \boxed{491.67\ {}^\circ\mathrm{R}}$$

F3.7(b) $n = 0.325\ \mathrm{g} \times \left(\dfrac{1\ \mathrm{mol}}{20.18\ \mathrm{g}}\right) = 0.0161\ \mathrm{mol}$

$$p = \frac{nRT}{V}\ [\mathrm{F.3}] = \frac{(0.0161\ \mathrm{mol})(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(293.15\ \mathrm{K})}{2.00\ \mathrm{dm^3}}\left(\frac{\mathrm{dm^3}}{10^{-3}\ \mathrm{m^3}}\right)$$

$$= 1.96 \times 10^4\ \mathrm{Pa} = \boxed{19.6\ \mathrm{kPa}}$$

F.4 Energy

F4.1(b) All objects in motion have the ability to do work during the process of slowing. That is, they have energy, or, more precisely, the energy possessed by a body because of its motion is its **kinetic energy**, E_k. The law of conservation of energy tells us that the kinetic energy of an object equals the work done on the object in order to change its motion from an initial (i) state of $v_\mathrm{i} = 0$ to a final (f) state of $v_\mathrm{f} = v$. For an object of mass m travelling at a speed v,

$$E_\mathrm{k} = \tfrac{1}{2}mv^2\ [\mathrm{F.4}]$$

The **potential energy**, E_p or more commonly V, of an object is the energy it possesses as a result of its position. For an object of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$V(h) = mgh\ [\mathrm{F.5}], \quad \text{where} \quad g = 9.81\ \mathrm{m\ s^{-2}}$$

Eqn F.5 assigns the gravitational potential energy at the surface of the Earth, $V(0)$, a value equal zero and g is called the **acceleration of free fall.**

The Coulomb potential energy describes the particularly important electrostatic interaction between two point charges Q_1 and Q_2 separated by the distance r:

$$V(r) = \frac{Q_1Q_2}{4\pi\varepsilon_0 r} \text{ in a vacuum [F.6, } \varepsilon_0 \text{ is the vacuum permittivity]}$$

and $V(r) = \dfrac{Q_1Q_2}{4\pi\varepsilon_\mathrm{r}\varepsilon_0 r}$ in a medium that has the relative permittivity ε_r (formerly, dielectric constant). Eqn F.6 assigns the Coulomb potential energy at infinite separation, $V(\infty)$, a value equal to zero. Convention assigns a negative value to the Coulomb potential energy when the interaction is attractive and a positive value when it is repulsive. The Coulomb potential energy and the force acting on the charges are related by the expression $F = -\mathrm{d}V/\mathrm{d}r$.

4.2(b) The law of conservation of energy requires that the minimum kinetic energy [F.4] required to reach height h equals the increase in gravitational potential energy [F.5]:

$$\begin{aligned} E_k &= mgh \\ &= (0.025\ \text{kg}) \times (9.81\ \text{m s}^{-2}) \times (50\ \text{m}) = 12\ \text{kg m}^2\,\text{s}^{-2} = \boxed{12\ \text{J}} \end{aligned}$$

4.3(b) The Coulomb potential, ϕ, is

$\phi = \dfrac{Q_2}{4\pi\varepsilon_0 r}$, where r is the separation of point charge Q_1 and the ion charge Q_2.

Q_1 interacts with two ions, which are treated as point charges in this exercise, and the interactions are additive:

$$\begin{aligned} \phi &= \left(\frac{Q_2}{4\pi\varepsilon_0 r}\right)_{\text{Na}^+} + \left(\frac{Q_2}{4\pi\varepsilon_0 r}\right)_{\text{Cl}^-} = \left(\frac{e}{4\pi\varepsilon_0 r}\right)_{\text{Na}^+} + \left(\frac{-e}{4\pi\varepsilon_0 r}\right)_{\text{Cl}^-} \\ &= \frac{e}{4\pi\varepsilon_0} \times \left\{\left(\frac{1}{r}\right)_{\text{Na}^+} - \left(\frac{1}{r}\right)_{\text{Cl}^-}\right\} \\ &= \left(\frac{1.6022 \times 10^{-19}\,\text{C}}{1.1127 \times 10^{-10}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1}}\right) \times \left(\frac{1}{10^{-12}\,\text{m}}\right) \times \left\{\left(\frac{1}{r/\text{pm}}\right)_{\text{Na}^+} - \left(\frac{1}{r/\text{pm}}\right)_{\text{Cl}^-}\right\} \\ &= (1440\ \text{V}) \times \left\{\left(\frac{1}{r/\text{pm}}\right)_{\text{Na}^+} - \left(\frac{1}{r/\text{pm}}\right)_{\text{Cl}^-}\right\} \quad [1\ \text{J C}^{-1} = 1\ \text{V}] \end{aligned}$$

Figure F.1 shows the positions of the sodium and chloride ions as the charge Q_1 approaches the centre point between the two ions along a straight line at the angle θ to the internuclear line. If we interpret the exercise as specifying that the approach be at the angle $\theta = 90°$, then $r_{\text{Na}^+} = r_{\text{Cl}^-}$ all along the approach and the above relationship tells us that $\boxed{\phi_{\theta=90°} = 0}$ at all values of r (defined in Figure F.1). For angles other than $\theta = 90°$, the above equation for ϕ can be computed as a function of r at fixed θ. The law of cosines is used to calculate the requisite values r_{Na^+} and r_{Cl^-} at each value of r and θ.

$$r_{\text{Na}^+} = (r_c^2 + r^2 - 2r_c r\cos\theta)^{1/2} \quad \text{and} \quad r_{\text{Cl}^-} = (r_c^2 + r^2 - 2r_c r\cos(\pi - \theta))^{1/2}$$

Plots of ϕ against r at $\theta = 30°$, 45°, and 60° are presented in Figure F.2. It is apparent that as Q_1 approaches the centre from infinity the Coulomb potential rises to a peak at about half the internuclear distance because of the dominate interaction with the sodium cation. On closer approach to the centre the influence of the chloride anion progressively increases, thereby causing a decline in the Coulomb potential until the interactions with the two ions is exactly balanced when Q_1 is midway between the ions (i.e. at $r = 0$).

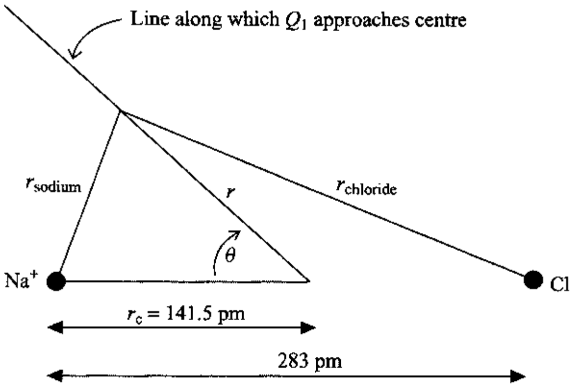


Figure F.1

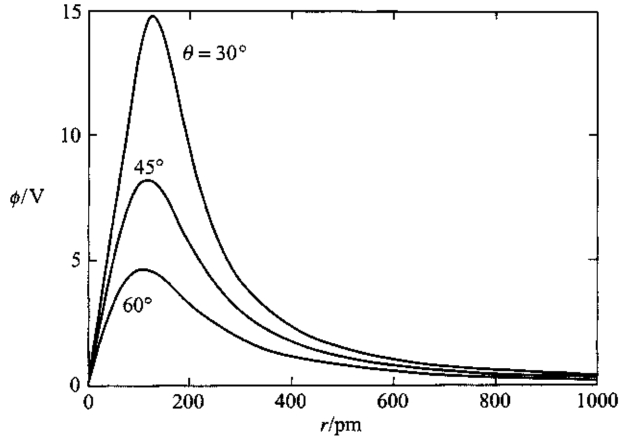


Figure F.2

F.5 The relationship between molecular and bulk properties

F5.1(b) The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules. Quantization is important for the electronic states of atoms and molecules and for both the rotational and vibrational states of molecules.

F5.2(b)
$$\lim_{T\to 0}\left(\frac{N_{\text{upper}}}{N_{\text{lower}}}\right) = \lim_{T\to 0}(\mathrm{e}^{-\Delta E/kT})\,[\text{F.9}] = \mathrm{e}^{-\infty} = 0$$

$$\lim_{T\to \infty}\left(\frac{N_{\text{upper}}}{N_{\text{lower}}}\right) = \lim_{T\to \infty}(\mathrm{e}^{-\Delta E/kT})\,[\text{F.9}] = \mathrm{e}^{-0} = 1$$

In the limit of the absolute zero of temperature, all particles occupy the lower state. The upper state is empty. In the limit of infinitely large temperature, all states are equally populated.

5.3(b) The Maxwell distribution of speeds indicates that a few molecules have either very low or very high speeds. Furthermore, the distribution peaks at lower speeds when either the temperature is low or the molecular mass is high. The distribution peaks at high speeds when either the temperature is high or the molecular mass is low.

5.4(b) Rates of chemical reaction typically increase with increasing temperature because more molecules have the requisite speed and corresponding kinetic energy to promote excitation and bond breakage during collision at the high temperatures.

5.5(b) $v_{\text{mean}} \propto (T/M)^{1/2}$ [F.11]

$$\frac{v_{\text{mean}}(T_2)}{v_{\text{mean}}(T_1)} = \frac{(T_2/M)^{1/2}}{(T_1/M)^{1/2}} = \left(\frac{T_2}{T_1}\right)^{1/2}$$

$$\frac{v_{\text{mean}}(303\ \text{K})}{v_{\text{mean}}(293\ \text{K})} = \left(\frac{303\ \text{K}}{293\ \text{K}}\right)^{1/2} = \boxed{1.02}$$

5.6(b) A gaseous helium atom has three translational degrees of freedom (the components of motion in the x, y, and z directions). Consequently, the equipartition theorem assigns a mean energy of $\frac{3}{2}kT$ to each atom. The molar internal energy, U_{m}, is

$$U_{\text{m}} = \tfrac{3}{2}N_{\text{A}}kT = \tfrac{3}{2}RT\ [\text{F.10}] = \tfrac{3}{2}(8.3145\ \text{J mol}^{-1}\,\text{K}^{-1})(303\ \text{K}) = 3.78\ \text{kJ mol}^{-1}$$

$$U = nU_{\text{m}} = mM^{-1}U_{\text{m}} = (10.0\ \text{g})\left(\frac{1\ \text{mol}}{4.00\ \text{g}}\right)\left(\frac{3.78\ \text{kJ}}{\text{mol}}\right) = \boxed{9.45\ \text{kJ}}$$

5.7(b) A solid-state lead atom has three vibrational quadratic degrees of freedom (the components of vibrational motion in the x, y, and z directions). Its potential energy also has a quadratic form in each direction because $V \propto (x - x_{\text{eq}})^2$. There are a total of six quadratic degrees of freedom for the atom because the atoms have no translational or rotational motion. Consequently, the equipartition theorem assigns a mean energy of $\frac{6}{2}kT = 3kT$ to each atom. This is the **law of Dulong and Petit**. The molar internal energy, U_{m}, is

$$U_{\text{m}} = 3N_{\text{A}}kT = 3RT\ [\text{F.10}] = 3(8.3145\ \text{J mol}^{-1}\,\text{K}^{-1})(293\ \text{K}) = 7.31\ \text{kJ mol}^{-1}$$

$$U = nU_{\text{m}} = mM^{-1}U_{\text{m}} = (10.0\ \text{g})\left(\frac{1\ \text{mol}}{207.2\ \text{g}}\right)\left(\frac{7.31\ \text{kJ}}{\text{mol}}\right) = \boxed{0.353\ \text{kJ}}$$

F.6 The electromagnetic field

6.1(b) $$\nu = \frac{c}{\lambda}\ [\text{F.12}] = \frac{3.00 \times 10^{8}\ \text{m s}^{-1}}{720 \times 10^{-9}\ \text{m}} = 4.17 \times 10^{14}\ \text{s}^{-1} = \boxed{4.17 \times 10^{14}\ \text{Hz}}$$

6.2(b) $$\tilde{\nu} = \frac{\nu}{c}\ [\text{F.13}] = \frac{160 \times 10^{6}\ \text{s}^{-1}}{3.00 \times 10^{8}\ \text{m s}^{-1}} = \boxed{0.533\ \text{m}^{-1}}$$

F6.3(b) (a) $\tilde{\nu} = \dfrac{1}{\lambda}\,[\text{F.13}] = \dfrac{1}{3.0\ \text{cm}} = \boxed{0.33\ \text{cm}^{-1}}$

(b) $\nu = \dfrac{c}{\lambda}\,[\text{F.12}] = \dfrac{3.00\times10^{8}\ \text{m s}^{-1}}{3.0\times10^{-2}\ \text{m}} = 1.0\times10^{10}\ \text{s}^{-1} = \boxed{10\ \text{GHz}}$

F.7 Units

F7.1(b) $1.45\ \text{dm}^3\left(\dfrac{10^2\ \text{cm}}{10\ \text{dm}}\right)^3 = \boxed{1.45\times10^3\ \text{cm}^3}$

F7.2(b) $\left(1.12\,\dfrac{\text{g}}{\text{dm}^3}\right)\times\left(\dfrac{1\ \text{kg}}{10^3\ \text{g}}\right)\times\left(\dfrac{1\ \text{dm}}{10^{-1}\ \text{m}}\right)^3 = \boxed{1.12\ \text{kg m}^{-3}}$

F7.3(b) $\dfrac{\text{J}^2}{\text{N}^3} = \dfrac{(\text{N m})^2}{\text{N}^3} = \dfrac{\text{m}^2}{\text{N}} = \dfrac{\text{m}^2}{\text{kg m s}^{-2}} = \boxed{\text{m kg}^{-1}\,\text{s}^2}$

F7.4(b) $\dfrac{kT}{e} = \dfrac{(1.381\times10^{-23}\ \text{C V K}^{-1})\times(298\ \text{K})}{1.602\times10^{-19}\ \text{C}}\left(\dfrac{\text{mV}}{10^{-3}\ \text{V}}\right) = \boxed{25.7\ \text{mV}}\ [1\ \text{J} = 1\ \text{C V}]$

$$kT = (1.381\times10^{-23}\ \text{J K}^{-1})\times(298\ \text{K}) = (4.11\times10^{-21}\ \text{J})\times\left(\frac{1\ \text{eV}}{1.602\times10^{-19}\ \text{J}}\right)$$

$$= 2.57\times10^{-2}\ \text{eV} = \boxed{25.7\ \text{meV}}$$

F7.5(b) $\left(\dfrac{8.3144\ \text{J}}{\text{K mol}}\right)\times\left(\dfrac{\text{Pa m}^3}{\text{J}}\right)\times\left(\dfrac{\text{cm}}{10^{-2}\ \text{m}}\right)^3\times\left(\dfrac{1\ \text{mol}}{6.022\times10^{23}\ \text{molecule}}\right)$

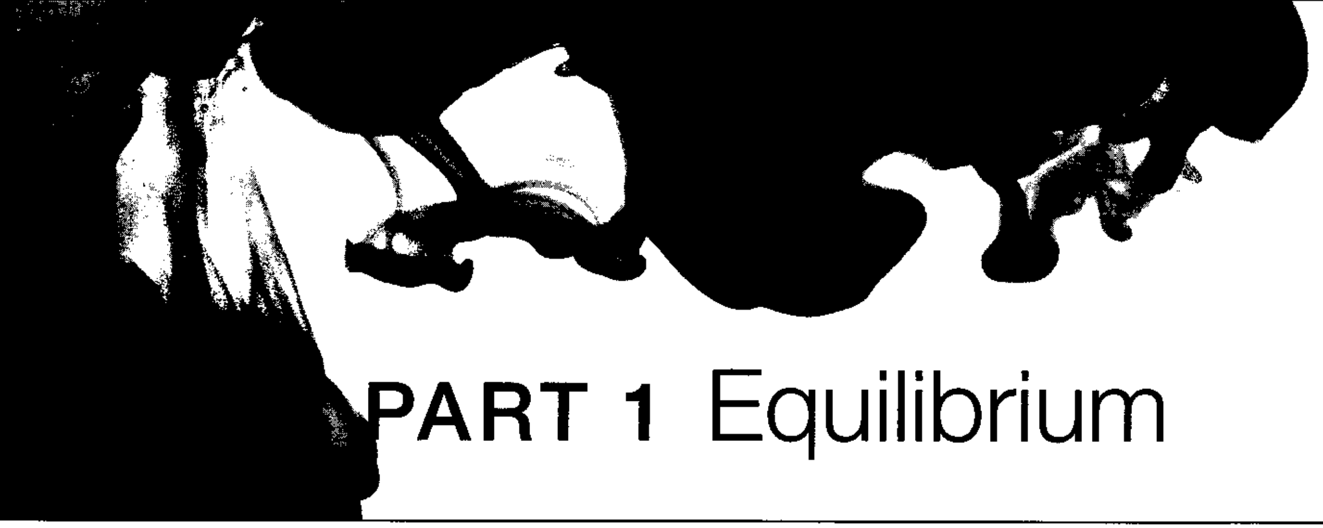
$= \boxed{1.381\times10^{-17}\ \text{Pa cm}^3\ \text{K}^{-1}\,\text{molecule}^{-1}}$

F7.6(b) $(1\ \text{J})\times\left(\dfrac{\text{Pa m}^3}{\text{J}}\right)\times\left(\dfrac{1\ \text{atm}}{101325\ \text{Pa}}\right)\times\left(\dfrac{\text{cm}}{10^{-2}\ \text{m}}\right)^3\times\left(\dfrac{\text{L}}{10^3\ \text{cm}^3}\right) = \boxed{9.869\times10^{-3}\ \text{atm L}}$

F7.7(b) (a) Base unit of μ_B = Base unit of $\dfrac{e\hbar}{2m_e} = \left(\dfrac{\text{C J s}}{\text{kg}}\right)\times\left(\dfrac{\text{kg m}^2\,\text{s}^{-2}}{\text{J}}\right) = \text{C m}^2\,\text{s}^{-1}$

Base unit of $\dfrac{\mu_B^2}{\mu_0 r^3} = \left(\dfrac{(\text{C m}^2\,\text{s}^{-1})^2}{(\text{J s}^2\,\text{C}^{-2}\,\text{m}^{-1})\times(\text{m}^3)}\right)\times\left(\dfrac{\text{J}}{\text{kg m}^2\,\text{s}^{-2}}\right) = \boxed{\text{C}^4\,\text{kg}^{-1}\,\text{s}^{-2}}$

(b) Unit of $\dfrac{\mu_B^2}{\mu_0 r^3} = (\text{C}^4\,\text{kg}^{-1}\,\text{s}^{-2})\times\left(\dfrac{\text{J}}{\text{C V}}\right)^4 = \boxed{\text{J}^4\,\text{V}^{-4}\,\text{kg}^{-1}\,\text{s}^{-2}}$



PART 1 Equilibrium

1

The properties of gases

Answers to discussion questions

D1.2 The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. Dalton's law is a limiting law because it holds exactly only under conditions where the gases have no effect on each other. This can only be true in the limit of zero pressure where the molecules of the gas are very far apart. Hence, Dalton's law holds exactly only for a mixture of perfect gases; for real gases, the law is only an approximation.

D1.4 The critical constants represent the state of a system at which the distinction between the liquid and vapour phases disappears. We usually describe this situation by saying that above the critical temperature the liquid phase cannot be produced by the application of pressure alone. The liquid and vapour phases can no longer coexist, although supercritical fluids have both liquid and vapour characteristics.

D1.6 The van der Waals equation is a cubic equation in the volume, V. Every cubic equation has some values of the coefficients for which the number of real roots passes from three to one. In fact, any equation of state of odd degree $n > 1$ can in principle account for critical behaviour because for equations of odd degree in V there are necessarily some values of temperature and pressure for which the number of real roots of V passes from n to 1. That is, the multiple values of V converge from n to 1 as the temperature approaches the critical temperature. This mathematical result is consistent with passing from a two-phase region (more than one volume for a given T and p) to a one-phase region (only one V for a given T and p), and this corresponds to the observed experimental result as the critical point is reached.

Solutions to exercises

E1.1(b) (a) The perfect gas law [1.8] is

$$pV = nRT$$

implying that the pressure would be

$$p = \frac{nRT}{V}$$

All quantities on the right are given to us except n, which can be computed from the given mass of Ar.

$$n = \frac{25\ \mathrm{g}}{39.95\ \mathrm{g\ mol^{-1}}} = 0.62\bar{6}\ \mathrm{mol}$$

$$\text{so}\quad p = \frac{(0.62\bar{6}\ \mathrm{mol}) \times (8.31 \times 10^{-2}\ \mathrm{dm^3\ bar\ K^{-1}\ mol^{-1}}) \times (30 + 273\ \mathrm{K})}{1.5\ \mathrm{dm^3}} = \boxed{10.\bar{5}\ \mathrm{bar}}$$

not 2.0 bar.

(b) The van der Waals equation [1.21a] is

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

$$\text{so}\quad p = \frac{(8.31 \times 10^{-2}\ \mathrm{dm^3\ bar\ K^{-1}\ mol^{-1}}) \times (30 + 273)\ \mathrm{K}}{(1.5\ \mathrm{dm^3}/0.62\bar{6}\ \mathrm{mol}) - 3.20 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}}}$$

$$- \frac{(1.337\ \mathrm{dm^6\ atm\ mol^{-2}}) \times (1.013\ \mathrm{bar\ atm^{-1}})}{(1.5\ \mathrm{dm^3}/0.62\bar{6}\ \mathrm{mol})^2} = \boxed{10.\bar{4}\ \mathrm{bar}}$$

E1.2(b) (a) Boyle's law [1.5] applies.

$$pV = \text{constant} \quad \text{so} \quad p_\mathrm{f}V_\mathrm{f} = p_\mathrm{i}V_\mathrm{i}$$

This equation can be solved for either initial or final pressure, hence

$$p_\mathrm{i} = \frac{p_\mathrm{f}V_\mathrm{f}}{V_\mathrm{i}} = \frac{(1.97\ \mathrm{bar}) \times (2.14\ \mathrm{dm^3})}{(2.14 + 1.80)\ \mathrm{dm^3}} = \boxed{1.07\ \mathrm{bar}}$$

(b) The original pressure in Torr is

$$p_\mathrm{i} = (1.07\ \mathrm{bar}) \times \left(\frac{1\ \mathrm{atm}}{1.013\ \mathrm{bar}}\right) \times \left(\frac{760\ \mathrm{Torr}}{1\ \mathrm{atm}}\right) = \boxed{803\ \mathrm{Torr}}$$

E1.3(b) The relationship between pressure and temperature at constant volume can be derived from the perfect gas law, $pV = nRT$ [1.8]

$$\text{so}\quad p \propto T \quad \text{and} \quad \frac{p_\mathrm{i}}{T_\mathrm{i}} = \frac{p_\mathrm{f}}{T_\mathrm{f}}$$

The final pressure, then, ought to be

$$p_\mathrm{f} = \frac{p_\mathrm{i}T_\mathrm{f}}{T_\mathrm{i}} = \frac{(125\ \mathrm{kPa}) \times (11 + 273)\ \mathrm{K}}{(23 + 273)\ \mathrm{K}} = \boxed{120\ \mathrm{kPa}}$$

E1.4(b) According to the perfect gas law [1.8], one can compute the amount of gas from pressure, temperature, and volume.

$$pV = nRT$$

$$\text{so}\quad n = \frac{pV}{RT} = \frac{(1.00\ \mathrm{atm}) \times (1.013 \times 10^5\ \mathrm{Pa\ atm^{-1}}) \times (4.00 \times 10^3\ \mathrm{m^3})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (20 + 273)\ \mathrm{K}} = 1.66 \times 10^5\ \mathrm{mol}$$

Once this is done, the mass of the gas can be computed from the amount and the molar mass:

$$m = (1.66 \times 10^5\ \text{mol}) \times (16.04\ \text{g mol}^{-1}) = 2.67 \times 10^6\ \text{g} = \boxed{2.67 \times 10^3\ \text{kg}}$$

E1.5(b) Use the equation for hydrostatic pressure [1.3], $p = p_{\text{ex}} + \rho gh$. Let p_{ex} be the pressure at the top of the straw and p is the pressure on the surface of the liquid (atmospheric pressure). Thus, the pressure difference is

$$p - p_{\text{ex}} = \rho gh = (1.0\ \text{g cm}^{-3}) \times \frac{1\ \text{kg}}{10^3\ \text{g}} \times \left(\frac{1\ \text{cm}}{10^{-2}\ \text{m}}\right)^3 \times (9.81\ \text{m s}^{-2}) \times (0.15\ \text{m})$$

$$= \boxed{1.5 \times 10^3\ \text{Pa}} = 1.5 \times 10^{-2}\ \text{atm}$$

E1.6(b) The pressure in the apparatus is given by

$$p = p_{\text{ex}} + \rho gh\ [1.3]$$

where $p_{\text{ex}} = 760\ \text{Torr} = 1\ \text{atm} = 1.013 \times 10^5\ \text{Pa}$,

and $$\rho gh = 13.55\ \text{g cm}^{-3} \times \left(\frac{1\ \text{kg}}{10^3\ \text{g}}\right) \times \left(\frac{1\ \text{cm}}{10^{-2}\ \text{m}}\right)^3 \times 0.100\ \text{m} \times 9.806\ \text{m s}^{-2} = 1.33 \times 10^4\ \text{Pa}$$

$$p = 1.013 \times 10^5\ \text{Pa} + 1.33 \times 10^4\ \text{Pa} = 1.146 \times 10^5\ \text{Pa} = \boxed{115\ \text{kPa}}$$

E1.7(b) Rearrange the perfect gas equation [1.8] to give $R = \dfrac{pV}{nT} = \dfrac{pV_{\text{m}}}{T}$

All gases are perfect in the limit of zero pressure. Therefore, the value of pV_{m}/T extrapolated to zero pressure will give the best value of R.

The molar mass can be introduced through

$$pV = nRT = \frac{m}{M}RT$$

which on rearrangement gives $M = \dfrac{m}{V}\dfrac{RT}{p} = \rho\dfrac{RT}{p}$.

The best value of M is obtained from an extrapolation of ρ/p versus p to zero pressure; the intercept is M/RT.

Draw up the following table:

p/atm	$(pV_{\text{m}}/T)/(\text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})$	$(\rho/p)/(\text{g dm}^{-3}\ \text{atm}^{-1})$
0.750 000	0.082 0014	1.428 59
0.500 000	0.082 0227	1.428 22
0.250 000	0.082 0414	1.427 90

From Figure 1.1(a), $\left(\dfrac{pV_{\text{m}}}{T}\right)_{p=0} = \boxed{0.082\,062\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}}$

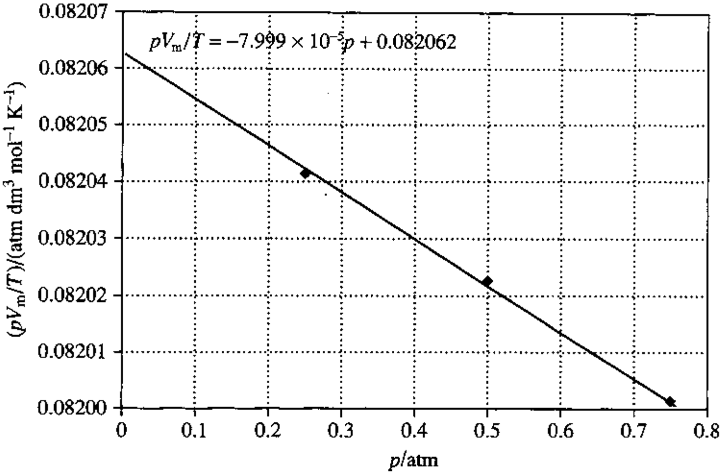


Figure 1.1(a)

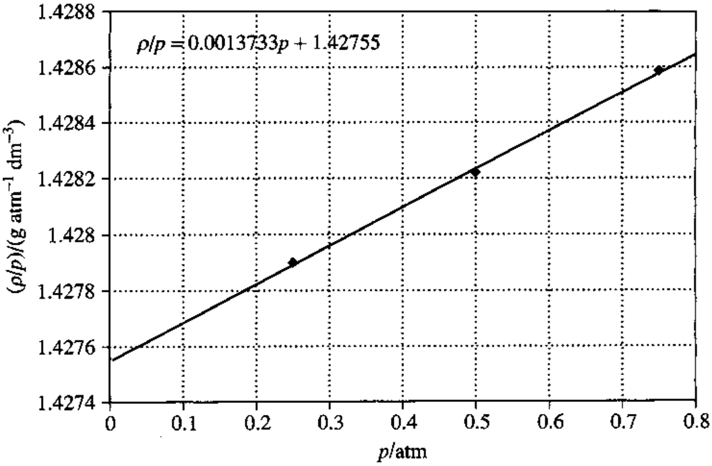


Figure 1.1(b)

From Figure 1.1(b), $\left(\dfrac{\rho}{p}\right)_{p=0} = 1.427\,55\text{ g dm}^{-3}\text{ atm}^{-1}$.

$$M = RT\left(\frac{\rho}{p}\right)_{p=0} = (0.082062\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}) \times (273.15\text{ K}) \times (1.42755\text{ g dm}^{-3}\text{ atm}^{-1})$$

$$= \boxed{31.9988\text{ g mol}^{-1}}$$

The value obtained for R deviates from the accepted value by 0.005%, better than can be expected from a linear extrapolation from three data points.

E1.8(b) The mass density ρ is related to the molar volume V_m by

$$V_m = \frac{V}{n} = \frac{V}{m} \times \frac{m}{n} = \frac{M}{\rho}$$

where M is the molar mass. Putting this relationship into the perfect gas law [1.8] yields

$$pV_{\mathrm{m}} = RT \quad \text{so} \quad \frac{pM}{\rho} = RT$$

Rearranging this result gives an expression for M; once we know the molar mass, we can divide by the molar mass of phosphorus atoms to determine the number of atoms per gas molecule.

$$M = \frac{RT\rho}{p} = \frac{(8.3145\ \mathrm{Pa\ m^3\ mol^{-1}}) \times [(100 + 273)\ \mathrm{K}] \times (0.6388\ \mathrm{kg\ m^{-3}})}{1.60 \times 10^4\ \mathrm{Pa}}$$

$$= 0.124\ \mathrm{kg\ mol^{-1}} = 124\ \mathrm{g\ mol^{-1}}$$

The number of atoms per molecule is

$$\frac{124\ \mathrm{g\ mol^{-1}}}{31.0\ \mathrm{g\ mol^{-1}}} = 4.00$$

suggesting a formula of $\boxed{\mathrm{P_4}}$.

E1.9(b) Use the perfect gas equation [1.8] to compute the amount; then convert to mass:

$$pV = nRT \quad \text{so} \quad n = \frac{pV}{RT}$$

We need the partial pressure of water, which is 53% of the equilibrium vapour pressure at the given temperature and standard pressure. (We must look it up in a handbook like the *CRC Handbook of Chemistry and Physics* or another resource such as the *NIST Chemistry WebBook*.)

$$p = (0.53) \times (2.81 \times 10^3\ \mathrm{Pa}) = 1.49 \times 10^3\ \mathrm{Pa}$$

$$\text{so} \quad n = \frac{(1.49 \times 10^3\ \mathrm{Pa}) \times (250\ \mathrm{m^3})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (23 + 273)\ \mathrm{K}} = 151\ \mathrm{mol}$$

$$\text{and} \quad m = (151\ \mathrm{mol}) \times (18.0\ \mathrm{g\ mol^{-1}}) = 2.72 \times 10^3\ \mathrm{g} = \boxed{2.72\ \mathrm{kg}}$$

E1.10(b) (a) The volume occupied by each gas is the same, since each completely fills the container. Thus, solving for V we have (assuming a perfect gas)

$$V = \frac{n_{\mathrm{J}}RT}{p_{\mathrm{J}}}$$

We have the pressure of neon, so we focus on it

$$n_{\mathrm{Ne}} = \frac{0.225\ \mathrm{g}}{20.18\ \mathrm{g\ mol^{-1}}} = 1.11\bar{5} \times 10^{-2}\ \mathrm{mol}$$

Thus,

$$V = \frac{1.11\bar{5} \times 10^{-2}\ \mathrm{mol} \times 8.3145\ \mathrm{Pa\ m^3\ K^{-1}\ mol^{-1}} \times 300\ \mathrm{K}}{8.87 \times 10^3\ \mathrm{Pa}} = 3.14 \times 10^{-3}\ \mathrm{m^3} = \boxed{3.14\ \mathrm{dm^3}}$$

(b) The total pressure is determined from the total amount of gas, $n = n_{\mathrm{CH_4}} + n_{\mathrm{Ar}} + n_{\mathrm{Ne}}$.

$$n_{\mathrm{CH_4}}=\frac{0.320\ \mathrm{g}}{16.04\ \mathrm{g\ mol^{-1}}}=1.99\bar{5}\times10^{-2}\ \mathrm{mol}\qquad n_{\mathrm{Ar}}=\frac{0.175\ \mathrm{g}}{39.95\ \mathrm{g\ mol^{-1}}}=4.38\times10^{-3}\ \mathrm{mol}$$

$$n=(1.99\bar{5}+0.438+1.11\bar{5})\times10^{-2}\ \mathrm{mol}=3.55\times10^{-2}\ \mathrm{mol}$$

and $$p=\frac{nRT}{V}\,[1.8]=\frac{3.55\times10^{-2}\ \mathrm{mol}\times8.3145\ \mathrm{Pa\ m^3\ K^{-1}\ mol^{-1}}\times300\ \mathrm{K}}{3.14\times10^{-3}\ \mathrm{m^3}}$$

$$=\boxed{2.82\times10^{4}\ \mathrm{Pa}}=\boxed{28.2\ \mathrm{kPa}}$$

E1.11(b) This is similar to Exercise 1.11(a) with the exception that the density must first be calculated:

$$M=\rho\frac{RT}{p}\ [\text{Exercise 1.8(a)}]$$

$$\rho=\frac{33.5\times10^{-3}\ \mathrm{g}}{250\ \mathrm{cm^3}}\times\left(\frac{10^3\ \mathrm{cm^3}}{\mathrm{dm^3}}\right)=0.134\ \mathrm{g\ dm^{-3}}$$

$$M=\frac{(0.134\ \mathrm{g\ dm^{-3}})\times(62.36\ \mathrm{dm^3\ Torr\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{152\ \mathrm{Torr}}=\boxed{16.4\ \mathrm{g\ mol^{-1}}}$$

E1.12(b) This exercise is similar to Exercise 1.12(a) in that it uses the definition of absolute zero as that temperature at which the volume of a sample of gas would become zero if the substance remained a gas at low temperatures. The solution uses the experimental fact that the volume is a linear function of the Celsius temperature:

$$V=V_0+\alpha\theta,\quad \text{where}\quad V_0=20.00\ \mathrm{dm^3}\ \text{and}\ \alpha=0.0741\ \mathrm{dm^3\ {}^\circ C^{-1}}$$

At absolute zero, $V=0=V_0+\alpha\theta$

so $$\theta(\text{abs.zero})=-\frac{V_0}{\alpha}=-\frac{20.00\ \mathrm{dm^3}}{0.0741\ \mathrm{dm^3\ {}^\circ C^{-1}}}=\boxed{-270^\circ\mathrm{C}}$$

which is close to the accepted value of −273°C.

E1.13(b) (a) $$p=\frac{nRT}{V}\ [1.8]$$

(i) $$p=\frac{(1.0\ \mathrm{mol})\times(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})\times(273.15\ \mathrm{K})}{22.414\ \mathrm{dm^3}}=\boxed{1.0\ \mathrm{atm}}$$

(ii) $$p=\frac{(1.0\ \mathrm{mol})\times(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})\times(500\ \mathrm{K})}{0.150\ \mathrm{dm^3}}=\boxed{270\ \mathrm{atm}}\ \text{(2 sig. figures)}$$

(b) $$p=\frac{nRT}{V-nb}-\frac{an^2}{V^2}\ [1.21a]$$

From Table (1.6) for H_2S, $a=4.484\ \mathrm{dm^6\ atm\ mol^{-1}}$ and $b=0.0434\ \mathrm{dm^3\ mol^{-1}}$.

(i) $$p=\frac{(1.0\ \mathrm{mol})\times(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})\times(273.15\ \mathrm{K})}{22.414\ \mathrm{dm^3}-(1.0\ \mathrm{mol})\times(4.34\times10^{-2}\ \mathrm{dm^3\ mol^{-1}})}$$

$$-\frac{(4.484\ \mathrm{dm^6\ atm\ mol^{-2}})\times(1.0\ \mathrm{mol})^2}{(22.414\ \mathrm{dm^3})^2}=\boxed{0.99\ \mathrm{atm}}$$

(ii) $$p=\frac{(1.0\ \mathrm{mol})\times(0.08206\ \mathrm{dm^3\,atm\,mol^{-1}\,K^{-1}})\times(500\ \mathrm{K})}{0.150\ \mathrm{dm^3}-(1.0\ \mathrm{mol})\times(4.34\times10^{-2}\ \mathrm{dm^3\,mol^{-1}})}-\frac{(4.484\ \mathrm{dm^3\,atm\,mol^{-1}})\times(1.0\ \mathrm{mol})^2}{(0.150\ \mathrm{dm^3})^2}=\boxed{190\ \mathrm{atm}}\ \text{(2 sig. figures)}$$

E1.14(b) The conversions needed are as follows:

$$1\ \mathrm{atm}=1.013\times10^5\ \mathrm{Pa},\ 1\ \mathrm{Pa}=1\ \mathrm{kg\,m^{-1}\,s^{-2}},\ 1\ \mathrm{dm^6}=(10^{-1}\ \mathrm{m})^6=10^{-6}\ \mathrm{m^6},\ 1\ \mathrm{dm^3}=10^{-3}\ \mathrm{m^3}$$

Therefore,

$$a=1.32\ \mathrm{atm\,dm^6\,mol^{-2}}\times\frac{1.013\times10^5\ \mathrm{kg\,m^{-1}\,s^{-2}}}{1\ \mathrm{atm}}\times\frac{10^{-6}\ \mathrm{m^6}}{\mathrm{dm^6}}$$
$$=\boxed{1.34\times10^{-1}\ \mathrm{kg\,m^5\,s^{-2}\,mol^{-2}}}$$

and $b=0.0426\ \mathrm{dm^3\,mol^{-1}}\times\dfrac{10^{-3}\ \mathrm{m^3}}{\mathrm{dm^3}}=\boxed{4.26\times10^{-5}\ \mathrm{m^3\,mol^{-1}}}$

E1.15(b) The compression factor is

$$Z=\frac{pV_{\mathrm{m}}}{RT}[1.17]=\frac{V_{\mathrm{m}}}{V_{\mathrm{m}}^{\circ}}$$

(a) Because $V_{\mathrm{m}}=V_{\mathrm{m}}^{\circ}+0.12V_{\mathrm{m}}^{\circ}=(1.12)V_{\mathrm{m}}^{\circ}$, we have $Z=\boxed{1.12}$

$\boxed{\text{Repulsive}}$ forces dominate.

(b) The molar volume is

$$V=(1.12)V_{\mathrm{m}}^{\circ}=(1.12)\times\left(\frac{RT}{p}\right)$$

$$V=(1.12)\times\left(\frac{(0.08206\ \mathrm{dm^3\,atm\,mol^{-1}\,K^{-1}})\times(350\ \mathrm{K})}{12\ \mathrm{atm}}\right)=\boxed{2.7\ \mathrm{dm^3\,mol^{-1}}}$$

E1.16(b) (a) $$V_{\mathrm{m}}^{\circ}=\frac{RT}{p}=\frac{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\ \mathrm{K})}{(200\ \mathrm{bar})\times(10^5\ \mathrm{Pa\,bar^{-1}})}$$
$$=1.24\times10^{-4}\ \mathrm{m^3\,mol^{-1}}=\boxed{0.124\ \mathrm{dm^3\,mol^{-1}}}$$

(b) The van der Waals equation is a cubic equation in V_{m}. The most direct way of obtaining the molar volume would be to solve the cubic analytically. However, this approach is cumbersome, so we proceed as in Example 1.4. The van der Waals equation is rearranged to the cubic form

$$V_{\mathrm{m}}^3-\left(b+\frac{RT}{p}\right)V_{\mathrm{m}}^2+\left(\frac{a}{p}\right)V_{\mathrm{m}}-\frac{ab}{p}=0\quad\text{or}\quad x^3-\left(b+\frac{RT}{p}\right)x^2+\left(\frac{a}{p}\right)x-\frac{ab}{p}=0$$

with $x=V_{\mathrm{m}}/(\mathrm{dm^3\,mol^{-1}})$.

The coefficients in the equation are

$$b+\frac{RT}{p}=(3.19\times10^{-2}\,\mathrm{dm^3\,mol^{-1}})+\frac{(0.08206\,\mathrm{dm^3\,atm\,mol^{-1}\,K^{-1}})\times(298.15\,\mathrm{K})}{(200\,\mathrm{bar})\times(1.013\,\mathrm{atm\,bar^{-1}})}$$
$$=(3.19\times10^{-2}+0.120\overline{8})\,\mathrm{dm^3\,mol^{-1}}=0.152\overline{7}\,\mathrm{dm^3\,mol^{-1}}$$

$$\frac{a}{p}=\frac{1.364\,\mathrm{dm^6\,atm\,mol^{-2}}}{(200\,\mathrm{bar})\times(1.013\,\mathrm{atm\,bar^{-1}})}=6.73\times10^{-3}\,\mathrm{dm^6\,mol^{-2}}$$

$$\frac{ab}{p}=\frac{(1.364\,\mathrm{dm^6\,atm\,mol^{-2}})\times(3.19\times10^{-2}\,\mathrm{dm^3\,mol^{-1}})}{(200\,\mathrm{bar})\times(1.013\,\mathrm{atm\,bar^{-1}})}=2.14\overline{8}\times10^{-4}\,\mathrm{dm^9\,mol^{-3}}$$

Thus, the equation to be solved is $x^3-0.152\overline{7}x^2+(6.73\times10^{-3})x-(2.14\overline{8}\times10^{-4})=0$.

Calculators and computer software for the solution of polynomials are readily available. In this case we find

$$x=0.109\quad\text{and}\quad V_\mathrm{m}=\boxed{0.109\,\mathrm{dm^3\,mol^{-1}}}$$

The difference is about 15%.

E1.17(b) The molar volume is obtained by solving $Z=\dfrac{pV_\mathrm{m}}{RT}$ [1.17], for V_m, which yields

$$V_\mathrm{m}=\frac{ZRT}{p}=\frac{(0.86)\times(0.08206\,\mathrm{dm^3\,atm\,mol^{-1}\,K^{-1}})\times(300\,\mathrm{K})}{20\,\mathrm{atm}}=1.0\overline{6}\,\mathrm{dm^3\,mol^{-1}}$$

(a) Then, $V=nV_\mathrm{m}=(8.2\times10^{-3}\,\mathrm{mol})\times(1.0\overline{6}\,\mathrm{dm^3\,mol^{-1}})=8.7\times10^{-3}\,\mathrm{dm^3}=\boxed{8.7\,\mathrm{cm^3}}$

(b) An approximate value of B can be obtained from eqn 1.19b by truncation of the series expansion after the second term, B/V_m, in the series. Then,

$$B=V_\mathrm{m}\left(\frac{pV_\mathrm{m}}{RT}-1\right)=V_\mathrm{m}\times(Z-1)=(1.0\overline{6}\,\mathrm{dm^3\,mol^{-1}})\times(0.86-1)=\boxed{-0.15\,\mathrm{dm^3\,mol^{-1}}}$$

E1.18(b) (a) Mole fractions are

$$x_\mathrm{N}=\frac{n_\mathrm{N}}{n_\mathrm{total}}\,[1.14]=\frac{2.5\,\mathrm{mol}}{(2.5+1.5)\,\mathrm{mol}}=\boxed{0.63}$$

Similarly, $x_\mathrm{H}=\boxed{0.37}$

(c) According to the perfect gas law

$$p_\mathrm{total}V=n_\mathrm{total}RT$$

so $$p_\mathrm{total}=\frac{n_\mathrm{total}RT}{V}=\frac{(4.0\,\mathrm{mol})\times(0.08206\,\mathrm{dm^3\,atm\,mol^{-1}\,K^{-1}})\times(273.15\,\mathrm{K})}{22.4\,\mathrm{dm^3}}=\boxed{4.0\,\mathrm{atm}}$$

(b) The partial pressures are

$$p_\mathrm{N}=x_\mathrm{N}p_\mathrm{tot}=(0.63)\times(4.0\,\mathrm{atm})=\boxed{2.5\,\mathrm{atm}}$$

and $p_\mathrm{H}=(0.37)\times(4.0\,\mathrm{atm})=\boxed{1.5\,\mathrm{atm}}$

1.19(b) The critical volume of a van der Waals gas is $V_c = 3b$

so $b = \frac{1}{3}V_c = \frac{1}{3}(148\ \text{cm}^3\ \text{mol}^{-1}) = 49.3\ \text{cm}^3\ \text{mol}^{-1} = \boxed{0.0493\ \text{dm}^3\ \text{mol}^{-1}}$

By interpreting b as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e. twice their radius); that volume times the Avogadro constant is the molar excluded volume b

$$b = N_A\left(\frac{4\pi(2r)^3}{3}\right) \quad \text{so} \quad r = \frac{1}{2}\left(\frac{3b}{4\pi N_A}\right)^{1/3}$$

$$r = \frac{1}{2}\left(\frac{3(49.3\ \text{cm}^3\ \text{mol}^{-1})}{4\pi(6.022\times10^{23}\ \text{mol}^{-1})}\right)^{1/3} = 1.35\times10^{-8}\ \text{cm} = \boxed{1.35\times10^{-10}\ \text{m}}$$

The critical pressure is $p_c = \dfrac{a}{27b^2}$

so $a = 27p_cb^2 = 27(48.20\ \text{atm})\times(0.0493\ \text{dm}^3\ \text{mol}^{-1})^2 = \boxed{3.16\ \text{dm}^6\ \text{atm mol}^{-2}}$

But this problem is overdetermined. We have another piece of information:

$$T_c = \frac{8a}{27Rb}$$

According to the constants we have already determined, T_c should be

$$T_c = \frac{8(3.16\ \text{dm}^6\ \text{atm mol}^{-2})}{27(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1})\times(0.0493\ \text{dm}^3\ \text{mol}^{-1})} = 231\ \text{K}$$

However, the reported T_c is 305.4 K, suggesting that our computed a/b is about 25% lower than it should be.

E1.20(b) (a) The Boyle temperature is the temperature at which $\lim\limits_{V_m\to\infty}\dfrac{dZ}{d(1/V_m)}$ vanishes. According to the van der Waals equation

$$Z = \frac{pV_m}{RT} = \frac{\left(\dfrac{RT}{V_m-b} - \dfrac{a}{V_m^2}\right)V_m}{RT} = \frac{V_m}{V_m-b} - \frac{a}{V_mRT}$$

so
$$\frac{dZ}{d(1/V_m)} = \left(\frac{dZ}{dV_m}\right)\times\left(\frac{dV_m}{d(1/V_m)}\right)$$

$$= -V_m^2\left(\frac{dZ}{dV_m}\right) = -V_m^2\left(\frac{-V_m}{(V_m-b)^2} + \frac{1}{V_m-b} + \frac{a}{V_m^2RT}\right)$$

$$= \frac{V_m^2b}{(V_m-b)^2} - \frac{a}{RT}$$

In the limit of large molar volume, we have

$$\lim_{V_m\to\infty}\frac{dZ}{d(1/V_m)} = b - \frac{a}{RT} = 0 \quad \text{so} \quad \frac{a}{RT} = b$$

and $$T = \frac{a}{Rb} = \frac{(4.484\ \mathrm{dm^6\ atm\ mol^{-2}})}{(0.08206\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}) \times (0.0434\ \mathrm{dm^3\ mol^{-1}})} = \boxed{1259\ \mathrm{K}}$$

(b) As in Exercise 1.19(b)

$$b = N_A\left(\frac{4\pi(2r)^3}{3}\right) \quad \text{so} \quad r = \frac{1}{2}\left(\frac{3b}{4\pi N_A}\right)^{1/3}$$

$$r = \frac{1}{2}\left(\frac{3(0.0434\ \mathrm{dm^3\ mol^{-1}})}{4\pi(6.022\times10^{23}\ \mathrm{mol^{-1}})}\right)^{1/3} = 1.29\times10^{-9}\,\mathrm{dm} = 1.29\times10^{-10}\,\mathrm{m} = \boxed{0.129\ \mathrm{nm}}$$

E1.21(b) States that have the same reduced pressure, temperature, and volume are said to correspond. The reduced pressure and temperature for N_2 at 1.0 atm and 25°C are

$$p_r = \frac{p}{p_c} = \frac{1.0\ \mathrm{atm}}{33.54\ \mathrm{atm}} = 0.030 \quad \text{and} \quad T_r = \frac{T}{T_c} = \frac{(25+273)\ \mathrm{K}}{126.3\ \mathrm{K}} = 2.36\ [1.24, \text{Table 1.5}]$$

The corresponding states are

(a) For H_2S

$$p = p_r p_c = (0.030)\times(88.3\ \mathrm{atm}) = \boxed{2.6\ \mathrm{atm}}$$

$$T = T_r T_c = (2.36)\times(373.2\ \mathrm{K}) = \boxed{881\ \mathrm{K}}$$

(Critical constants of H_2S obtained from *CRC Handbook of Chemistry and Physics.*)

(b) For CO_2

$$p = p_r p_c = (0.030)\times(72.85\ \mathrm{atm}) = \boxed{2.2\ \mathrm{atm}}$$

$$T = T_r T_c = (2.36)\times(304.2\,\mathrm{K}) = \boxed{718\ \mathrm{K}}$$

(c) For Ar

$$p = p_r p_c = (0.030)\times(48.00\ \mathrm{atm}) = \boxed{1.4\ \mathrm{atm}}$$

$$T = T_r T_c = (2.36)\times(150.72\ \mathrm{K}) = \boxed{356\ \mathrm{K}}$$

E1.22(b) The van der Waals equation is

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}\ [1.21\mathrm{b}]$$

which can be solved for b

$$b = V_m - \frac{RT}{p + \dfrac{a}{V_m^2}} = 4.00\times10^{-4}\,\mathrm{m^3\ mol^{-1}} - \frac{(8.3145\ \mathrm{J\ K^{-1}\,mol^{-1}})\times(288\ \mathrm{K})}{4.0\times10^6\ \mathrm{Pa} + \left(\dfrac{0.76\ \mathrm{m^6\ Pa\ mol^{-2}}}{(4.00\times10^{-4}\,\mathrm{m^3\ mol^{-1}})^2}\right)}$$

$$= \boxed{1.3\times10^{-4}\,\mathrm{m^3\ mol^{-1}}}$$

The compression factor is

$$Z = \frac{pV_m}{RT}\,[1.17] = \frac{(4.0\times10^6\,\text{Pa})\times(4.00\times10^{-4}\,\text{m}^3\,\text{mol}^{-1})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(288\,\text{K})} = \boxed{0.67}$$

Solutions to problems

Solutions to numerical problems

P1.2 Solving for n from the perfect gas equation [1.8] yields $n = \frac{pV}{RT}$. From the definition of molar mass $n = \frac{m}{M}$, hence $\rho = \frac{m}{V} = \frac{Mp}{RT}$. Rearrangement yields the desired relationship, namely $\boxed{p = \rho\frac{RT}{M}}$.

Therefore, for ideal gases $\frac{p}{\rho} = \frac{RT}{M}$ and $M = \frac{RT}{p/\rho}$. For real gases, find the zero-pressure limit of $\frac{p}{\rho}$ by plotting it against p. Draw up the following table. Bear in mind that 1 kPa = 10^3 kg m^{-1} s^{-2}.

p/(kPa)	12.223	25.20	36.97	60.37	85.23	101.3
ρ/(kg m^{-3})	0.225	0.456	0.664	1.062	1.468	1.734
$\frac{p/\rho}{10^3\,\text{m}^2\,\text{s}^{-2}}$	54.3	55.3	55.7	56.8	58.1	58.4

$\frac{p}{\rho}$ is plotted in Figure 1.2. A straight line fits the data rather well. The extrapolation to $p = 0$ yields an intercept of 54.0×10^3 m^2 s^{-2}. Then,

$$M = \frac{RT}{5.40\times10^4\,\text{m}^2\,\text{s}^{-2}} = \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298.15\,\text{K})}{5.40\times10^4\,\text{m}^2\,\text{s}^{-2}}$$

$$= 0.0459\,\text{kg mol}^{-1} = \boxed{45.9\,\text{g mol}^{-1}}$$

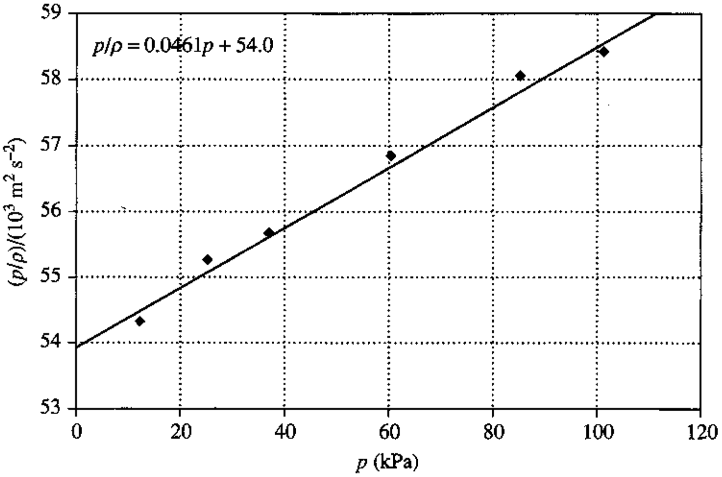


Figure 1.2

COMMENT. This method of the determination of the molar masses of gaseous compounds is due to Cannizarro, who presented it at the Karlsruhe conference of 1860, which had been called to resolve the problem of the determination of the molar masses of atoms and molecules and the molecular formulas of compounds.

P1.4 The mass of displaced gas is ρV, where V is the volume of the bulb and ρ is the density of the gas. The balance condition for the two gases is

$$m(\text{bulb}) = \rho V(\text{bulb}),\ m(\text{bulb}) = \rho' V(\text{bulb})$$

which implies that $\rho = \rho'$. Because [Problem 1.2] $\rho = \frac{pM}{RT}$, the balance condition is $pM = p'M'$, which implies that $M' = \frac{p}{p'} \times M$.

This relationship is valid in the limit of zero pressure (for a gas behaving perfectly).

In experiment 1, $p = 423.22$ Torr, $p' = 327.10$ Torr. Hence,

$$M' = \frac{423.22\ \text{Torr}}{327.10\ \text{Torr}} \times 70.014\ \text{g mol}^{-1} = 90.59\ \text{g mol}^{-1}$$

In experiment 2, $p = 427.22$ Torr, $p' = 293.22$ Torr, hence,

$$M' = \frac{427.22\ \text{Torr}}{293.22\ \text{Torr}} \times 70.014\ \text{g mol}^{-1} = 102.0\ \text{g mol}^{-1}$$

In a proper series of experiments one should reduce the pressure (e.g. by adjusting the balanced weight). Experiment 2 is closer to zero pressure than experiment 1, so it is more likely to be close to the true value:

$$\boxed{M' \approx 102\ \text{g mol}^{-1}}$$

The molecules CH_2FCF_3 and CHF_2CHF_2 have molar mass of 102 g mol^{-1}.

COMMENT. The substantial difference in molar mass between the two experiments ought to make us wary of confidently accepting the result of Experiment 2, even if it is the more likely estimate.

P1.6 We assume that no H_2 remains after the reaction has gone to completion. The balanced equation is

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3.$$

We can draw up the following table:

	N_2	H_2	NH_3	Total
Initial amount	n	n'	0	$n + n'$
Final amount	$n - \frac{1}{3}n'$	0	$\frac{2}{3}n'$	$n + \frac{1}{3}n'$
Specifically	0.33 mol	0	1.33 mol	1.66 mol
Mole fraction	0.20	0	0.80	1.00

$$p = \frac{nRT}{V} = (1.66\ \text{mol}) \times \left(\frac{(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}) \times (273.15\ \text{K})}{22.4\ \text{dm}^3}\right) = \boxed{1.66\ \text{atm}}$$

$$p(\text{H}_2) = x(\text{H}_2)p = \boxed{0}$$

$$p(\text{N}_2) = x(\text{N}_2)p = 0.20 \times 1.66\ \text{atm} = \boxed{0.33\ \text{atm}}$$

$$p(\text{NH}_3) = x(\text{NH}_3)p = 0.80 \times 1.66\ \text{atm} = \boxed{1.33\ \text{atm}}$$

P1.8 From the definition of Z [1.17] and the virial equation [1.19b], Z may be expressed in virial form as

$$Z = 1 + B\left(\frac{1}{V_\text{m}}\right) + C\left(\frac{1}{V_\text{m}}\right)^2 + \cdots$$

Since $V_\text{m} = \dfrac{RT}{p}$ [assumption of perfect gas], $\dfrac{1}{V_\text{m}} = \dfrac{p}{RT}$, hence on substitution and dropping terms beyond the second power of $\left(\dfrac{1}{V_\text{m}}\right)$

$$Z = 1 + B\left(\frac{p}{RT}\right) + C\left(\frac{p}{RT}\right)^2$$

$$Z = 1 + (-21.7 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}) \times \left(\frac{100\ \text{atm}}{(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}) \times (273\ \text{K})}\right)$$

$$+ (1.200 \times 10^{-3}\ \text{dm}^6\ \text{mol}^{-2}) \times \left(\frac{100\ \text{atm}}{(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}) \times (273\ \text{K})}\right)^2$$

$$Z = 1 - (0.0968) + (0.0239) = \boxed{0.927}$$

$$V_\text{m} = (0.927) \times \left(\frac{RT}{p}\right) = (0.927) \times \left(\frac{(0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (273\ \text{K})}{100\ \text{atm}}\right) = \boxed{0.208\ \text{dm}^3}$$

Question. What is the value of Z obtained from the next approximation using the value of V_m just calculated? Which value of Z is likely to be more accurate?

P1.10 Since $B'(T_\text{B}) = 0$ at the Boyle temperature [Section 1.3b], $B'(T_\text{B}) = a + be^{-c/T_\text{B}^2} = 0$

Solving for T_B: $T_\text{B} = \sqrt{\dfrac{-c}{\ln\left(\dfrac{-a}{b}\right)}} = \sqrt{\dfrac{-(1131\ \text{K}^2)}{\ln\left(\dfrac{-(-0.1993\ \text{bar}^{-1})}{(0.2002\ \text{bar}^{-1})}\right)}} = \boxed{5.0 \times 10^2\ \text{K}}$

P1.12 From Table 1.7 $T_\text{c} = \left(\dfrac{2}{3}\right) \times \left(\dfrac{2a}{3bR}\right)^{1/2}$, $p_\text{c} = \left(\dfrac{1}{12}\right) \times \left(\dfrac{2aR}{3b^3}\right)^{1/2}$

$\left(\dfrac{2a}{3bR}\right)^{1/2}$ may be solved for from the expression for p_c and yields $\left(\dfrac{12bp_\text{c}}{R}\right)$.

Thus, $T_c = \left(\frac{2}{3}\right) \times \left(\frac{12p_c b}{R}\right) = \left(\frac{8}{3}\right) \times \left(\frac{p_c V_c}{R}\right)$

$$= \left(\frac{8}{3}\right) \times \left(\frac{(40\ \text{atm}) \times (160 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1})}{0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}}\right) = \boxed{2\bar{1}0\ \text{K}}$$

By interpreting b as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e. twice their radius); that volume times the Avogadro constant is the molar excluded volume b

$$b = N_A\left(\frac{4\pi(2r)^3}{3}\right), \quad \text{so} \quad r = \frac{1}{2}\left(\frac{3b}{4\pi N_A}\right)^{1/3} \text{[Exercise 1.19(b)]} = \frac{1}{2}\left(\frac{V_c}{4\pi N_A}\right)^{1/3}$$

$$r = \frac{1}{2}\left(\frac{160\ \text{cm}^3\ \text{mol}^{-1}}{4\pi(6.022 \times 10^{23}\ \text{mol}^{-1})}\right)^{1/3} = 1.38 \times 10^{-8}\ \text{cm} = \boxed{0.138\ \text{nm}}$$

Solutions to theoretical problems

P1.14 Substitute the van der Waals equation [1.21b] into the definition of the compression factor [1.17]

$$Z = \frac{pV_m}{RT} = \frac{1}{\left(1 - \frac{b}{V_m}\right)} - \frac{a}{RTV_m} \text{ [Exercise 1.20(a)]}$$

which on expansion of $\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots$ yields

$$Z = 1 + \left(b - \frac{a}{RT}\right) \times \left(\frac{1}{V_m}\right) + b^2\left(\frac{1}{V_m}\right)^2 + \cdots$$

We note that all terms beyond the second are necessarily positive, so only if

$$\frac{a}{RTV_m} > \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots$$

can Z be less than one. If we ignore terms beyond $\frac{b}{V_m}$, the conditions are simply stated as

$$Z < 1 \quad \text{when } \frac{a}{RT} > b; \qquad Z > 1 \quad \text{when } \frac{a}{RT} < b$$

Thus, $Z < 1$ when attractive forces predominate and when there is insufficient thermal energy to disrupt those forces, and $Z > 1$ when size effects (short-range repulsions) predominate.

P1.16 The Dieterici equation is

$$p = \frac{RTe^{-a/RTV_m}}{V_m - b} \text{ [Table 1.7]}$$

At the critical point the derivatives of p with respect to V_m equal zero along the isotherm defined by $T = T_c$. This means that $(\partial p/\partial V_m)_T = 0$ and $(\partial^2 p/\partial V_m^2)_T = 0$ at the critical point.

$$\left(\frac{\partial p}{\partial V_m}\right)_T = p\left\{\frac{aV_m - ab - RTV_m^2}{V_m^2(V_m - b)(RT)}\right\}$$

and $$\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = \left(\frac{\partial p}{\partial V_m}\right)_T \left\{\frac{aV_m - ab - RTV_m^2}{V_m^2(V_m - b)(RT)}\right\} + p\frac{(-2aV_m^2 + 4V_m ab + RTV_m^3 - 2ab^2)}{\{V_m^3[(V_m - b)^2(RT)]\}}$$

Setting the Dieterici equation equal to the critical pressure and making the two derivatives vanish at the critical point yields three equations:

$$p_c = \frac{RT_c e^{-a/RT_cV_c}}{V_c - b}; \qquad aV_c - ab - RT_cV_c^2 = 0$$

$$-2aV_c^2 + 4V_c ab + RT_cV_c^3 - 2ab^2 = 0$$

Solving the middle equation for T_c, substitution of the result into the last equation, and solving for V_c yields the result

$$V_c = 2b \quad \text{or} \quad b = V_c/2$$

(The solution $V_c = b$ is rejected because there is a singularity in the Dieterici equation at the point $V_m = b$.) Substitution of $V_c = 2b$ into the middle equation and solving for T_c gives the result

$$T_c = a/4bR \quad \text{or} \quad a = 2RT_cV_c$$

Substitution of $V_c = 2b$ and $T_c = a/4bR$ into the first equation gives

$$p_c = \frac{ae^{-2}}{4b^2} = \frac{2RT_c e^{-2}}{V_c}$$

The equations for V_c, T_c, p_c are substituted into the equation for the critical compression factor [1.23] to give

$$Z_c = \frac{p_cV_c}{RT_c} = 2e^{-2} = 0.2707.$$

This is significantly lower than the critical compression factor that is predicted by the van der Waals equation, $Z_c(\text{vdW}) = p_cV_c/RT_c = 3/8 = 0.3750$. Experimental values for Z_c are summarized in Table 1.5, where it is seen that the Dieterici equation prediction is often better.

1.18 $$\frac{pV_m}{RT} = 1 + B'p + C'p^2 + \cdots \ [1.19a]$$

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \ [1.19b]$$

Thus, $$B'p + C'p^2 + \cdots = \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots$$

Multiply through by V_m, replace pV_m by $RT\{1 + (B/V_m) + \cdots\}$, and equate coefficients of powers of $1/V_m$:

$$B'RT + \frac{BB'RT + C'R^2T^2}{V_{\mathrm{m}}} + \cdots = B + \frac{C}{V_{\mathrm{m}}} + \cdots$$

Hence, $B'RT = B$, implying that $\boxed{B' = \dfrac{B}{RT}}$

Also, $BB'RT + C'R^2T^2 = C = B^2 + C'R^2T^2$, implying that $\boxed{C' = \dfrac{C - B^2}{R^2T^2}}$

P1.20 Write $V_{\mathrm{m}} = f(T, p)$, then $\mathrm{d}V_{\mathrm{m}} = \left(\dfrac{\partial V_{\mathrm{m}}}{\partial T}\right)_p \mathrm{d}T + \left(\dfrac{\partial V_{\mathrm{m}}}{\partial p}\right)_T \mathrm{d}p$

Restricting the variations of T and p to those that leave V_{m} constant, that is $\mathrm{d}V_{\mathrm{m}} = 0$, we obtain

$$\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p = -\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_T \times \left(\frac{\partial p}{\partial T}\right)_{V_{\mathrm{m}}} = -\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T^{-1} \times \left(\frac{\partial p}{\partial T}\right)_{V_{\mathrm{m}}}$$

From the equation of state

$$\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T = -\frac{RT}{V_{\mathrm{m}}^2} - \frac{2(a+bT)}{V_{\mathrm{m}}^3} = -\frac{V_{\mathrm{m}}RT + 2(a+bT)}{V_{\mathrm{m}}^3}$$

and $$\left(\frac{\partial p}{\partial T}\right)_{V_{\mathrm{m}}} = \frac{R}{V_{\mathrm{m}}} + \frac{b}{V_{\mathrm{m}}^2} = \frac{RV_{\mathrm{m}} + b}{V_{\mathrm{m}}^2}$$

Substituting

$$\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p = \left(\frac{V_{\mathrm{m}}^3}{V_{\mathrm{m}}RT + 2(a+bT)}\right)\left(\frac{RV_{\mathrm{m}} + b}{V_{\mathrm{m}}^2}\right) = \frac{RV_{\mathrm{m}}^2 + bV_{\mathrm{m}}}{V_{\mathrm{m}}RT + 2(a+bT)}$$

From the equation of state, $a + bT = pV_{\mathrm{m}}^2 - RTV_{\mathrm{m}}$

Then, $$\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p = \frac{RV_{\mathrm{m}}^2 + bV_{\mathrm{m}}}{V_{\mathrm{m}}RT + 2pV_{\mathrm{m}}^2 - 2RTV_{\mathrm{m}}} = \boxed{\frac{RV_{\mathrm{m}} + b_{\mathrm{m}}}{2pV_{\mathrm{m}} - RT}}$$

P1.22 $Z = \dfrac{V_{\mathrm{m}}}{V_{\mathrm{m}}^{\circ}}$, where V_{m}° = the molar volume of a perfect gas

From the given equation of state

$$V_{\mathrm{m}} = b + \frac{RT}{p} = b + V_{\mathrm{m}}^{\circ}$$

For $V_{\mathrm{m}} = 10b$, we have $10b = b + V_{\mathrm{m}}^{\circ}$, so $V_{\mathrm{m}}^{\circ} = 9b$.

Then, $Z = \dfrac{10b}{9b} = \boxed{\dfrac{10}{9} = 1.11}$

P1.24 The virial equation is

$$pV_m = RT\left(1+\frac{B}{V_m}+\frac{C}{V_m^2}+\cdots\right)[1.19b]$$

or $$\frac{pV_m}{RT} = 1+\frac{B}{V_m}+\frac{C}{V_m^2}+\cdots$$

(a) If we assume that the series may be truncated after the B term, then a plot of $\frac{pV_m}{RT}$ vs $\frac{1}{V_m}$ will have B as its slope and 1 as its y-intercept. Transforming the data gives

p/MPa	V_m/(dm^3 mol^{-1})	$(1/V_m)$/(mol dm^{-3})	pV_m/RT
0.4000	6.2208	0.1608	0.9976
0.5000	4.9736	0.2011	0.9970
0.6000	4.1423	0.2414	0.9964
0.8000	3.1031	0.3223	0.9952
1.000	2.4795	0.4033	0.9941
1.500	1.6483	0.6067	0.9912
2.000	1.2328	0.8112	0.9885
2.500	0.98357	1.017	0.9858
3.000	0.81746	1.223	0.9832
4.000	0.60998	1.639	0.9782

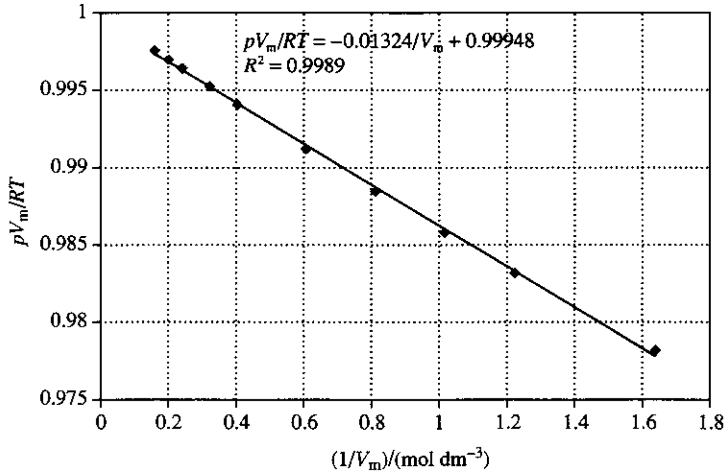


Figure 1.3(a)

The data are plotted in Figure 1.3(a). The data fit a straight line reasonably well, and the y-intercept is very close to 1. The regression yields $B = \boxed{-1.324\times10^{-2}\,\text{dm}^3\,\text{mol}^{-1}}$.

(b) A quadratic function fits the data somewhat better (Figure 1.3(b)) with a slightly better correlation coefficient and a y-intercept closer to 1. This fit implies that truncation of the virial series after the term with C is more accurate than after just the B term. The regression then yields

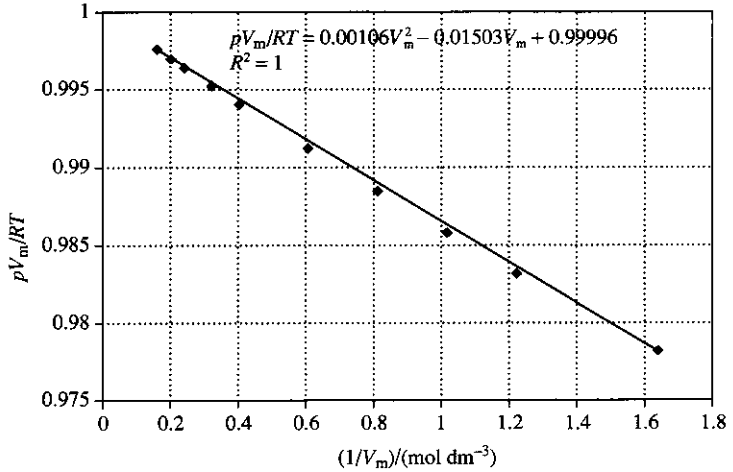


Figure 1.3(b)

$$B = \boxed{-1.503 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}} \quad \text{and} \quad C = \boxed{1.06 \times 10^{-3}\ \text{dm}^6\ \text{mol}^{-2}}$$

Solutions to applications

P1.26 The perfect gas law is $pV = nRT$

$$\text{so} \quad n = \frac{pV}{RT}$$

At mid-latitudes

$$n = \frac{(1.00\ \text{atm}) \times \{(1.00\ \text{dm}^2) \times (250 \times 10^{-3}\ \text{cm})/10\ \text{cm dm}^{-1}\}}{(0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (273\ \text{K})} = \boxed{1.12 \times 10^{-3}\ \text{mol}}$$

In the ozone hole

$$n = \frac{(1.00\ \text{atm}) \times \{(1.00\ \text{dm}^2) \times (100 \times 10^{-3}\ \text{cm})/10\ \text{cm dm}^{-1}\}}{(0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (273\ \text{K})} = \boxed{4.46 \times 10^{-4}\ \text{mol}}$$

The corresponding concentrations are

$$\frac{n}{V} = \frac{1.12 \times 10^{-3}\ \text{mol}}{(1.00\ \text{dm}^2) \times (40 \times 10^3\ \text{m}) \times (10\ \text{dm m}^{-1})} = \boxed{2.8 \times 10^{-9}\ \text{mol dm}^{-3}}$$

$$\text{and} \quad \frac{n}{V} = \frac{4.46 \times 10^{-4}\ \text{mol}}{(1.00\ \text{dm}^2) \times (40 \times 10^3\ \text{m}) \times (10\ \text{dm m}^{-1})} = \boxed{1.1 \times 10^{-9}\ \text{mol dm}^{-3}}$$

respectively.

P1.28 $n = \dfrac{pV}{RT}$ [1.8], $V = \dfrac{4\pi}{3}r^3 = \dfrac{4\pi}{3} \times (3.0\text{ m})^3 = 11\bar{3}\text{ m}^3 =$ volume of balloon

$p = 1.0$ atm, $T = 298$ K

(a) $$n = \frac{(1.0\text{ atm}) \times (11\bar{3} \times 10^3\text{ dm}^3)}{(0.08206\text{ dm}^3\text{ atm mol}^{-1}\text{ K}^{-1}) \times (298\text{ K})} = \boxed{4.6\bar{2} \times 10^3\text{ mol}}$$

(b) The mass that the balloon can lift is the difference between the mass of displaced air and the mass of the balloon. We assume that the mass of the balloon is essentially that of the gas it encloses:

$$m = m(\text{H}_2) = nM(\text{H}_2) = (4.6\bar{2} \times 10^3\text{ mol}) \times (2.02\text{ g mol}^{-1}) = 9.3\bar{3} \times 10^3\text{ g}$$

Mass of displaced air $= (11\bar{3}\text{ m}^3) \times (1.22\text{ kg m}^{-3}) = 1.3\bar{8} \times 10^2\text{ kg}$

Therefore, the mass of the maximum payload is

$$13\bar{8}\text{ kg} - 9.3\bar{3}\text{ kg} = \boxed{1.3 \times 10^2\text{ kg}}$$

(c) For helium, $m = nM(\text{He}) = (4.6\bar{2} \times 10^3\text{ mol}) \times (4.00\text{ g mol}^{-1}) = 18$ kg.

The maximum payload is now $13\bar{8}\text{ kg} - 18\text{ kg} = \boxed{1.2 \times 10^2\text{ kg}}$.

P1.30 Avogadro's principle states that equal volumes of gases contain equal amounts (moles) of the gases, so the volume mixing ratio is equal to the mole fraction. The definition of partial pressures is

$$p_\text{J} = x_\text{J}p$$

The perfect gas law is

$$pV = nRT \quad \text{so} \quad \frac{n_\text{J}}{V} = \frac{p_\text{J}}{RT} = \frac{x_\text{J}p}{RT}$$

(a) $$\frac{n(\text{CCl}_3\text{F})}{V} = \frac{(261 \times 10^{-12}) \times (1.0\text{ atm})}{(0.08206\text{ dm}^3\text{ atm K}^{-1}\text{mol}^{-1}) \times (10 + 273)\text{ K}} = \boxed{1.1 \times 10^{-11}\text{ mol dm}^{-3}}$$

and $$\frac{n(\text{CCl}_2\text{F}_2)}{V} = \frac{(509 \times 10^{-12}) \times (1.0\text{ atm})}{(0.08206\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}) \times (10 + 273)\text{ K}} = \boxed{2.2 \times 10^{-11}\text{ mol dm}^{-3}}$$

(b) $$\frac{n(\text{CCl}_3\text{F})}{V} = \frac{(261 \times 10^{-12}) \times (0.050\text{ atm})}{(0.08206\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}) \times (200\text{ K})} = \boxed{8.0 \times 10^{-13}\text{ mol dm}^{-3}}$$

and $$\frac{n(\text{CCl}_2\text{F}_2)}{V} = \frac{(509 \times 10^{-12}) \times (0.050\text{ atm})}{(0.08206\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}) \times (200\text{ K})} = \boxed{1.6 \times 10^{-12}\text{ mol dm}^{-3}}$$

2 The first law

Answers to discussion questions

D2.2 Rewrite the two expressions as follows:

(1) adiabatic $p \propto 1/V^{\gamma}$ (2) isothermal $p \propto 1/V$

The physical reason for the difference is that, in the isothermal expansion, energy flows into the system as heat and maintains the temperature despite the fact that energy is lost as work, whereas in the adiabatic case, where no heat flows into the system, the temperature must fall as the system does work. Therefore, the pressure must fall faster in the adiabatic process than in the isothermal case. Mathematically, this corresponds to $\gamma > 1$.

D2.4 The change in a state function is independent of the path taken between the initial and final states; hence for the calculation of the change in that function, any convenient path may be chosen. This may greatly simplify the computation involved and illustrates the power of thermodynamics.

The following list includes only those state functions that we have encountered in the first two chapters. More will be encountered in later chapters.

Temperature, pressure, volume, amount, energy, enthalpy, heat capacity, expansion coefficient, isothermal compressibility, Joule–Thomson coefficient.

D2.6 One can use the general expression for π_T given in *Further Information* 2.2 (and proved in Section 3.8, eqn 3.51) to derive its specific form for a van der Waals gas as given in Exercise 2.31(a), that is, $\pi_T = a/V_m^2$. (The derivation is carried out in Example 3.6.) For an isothermal expansion in a van der Waals gas $dU_m = (a/V_m)^2$. Hence, $\Delta U_m = -a(1/V_{m,2}) - 1/V_{m,1})$. See this derivation in the solution to Exercise 2.31(a). This formula corresponds to what one would expect for a real gas. As the molecules get closer and closer the molar volume gets smaller and smaller and the energy of attraction gets larger and larger.

Solutions to exercises

E2.1(b) The physical definition of work is $dw = -F\,dz$. [2.5]

In a gravitational field the force is the weight of the object, which is $F = mg$.

If g is constant over the distance the mass moves, dw may be integrated to give the total work

$$w = -\int_{z_i}^{z_f} F\,dz = -\int_{z_i}^{z_f} mg\,dz = -mg(z_f - z_i) = -mgh, \quad \text{where} \quad h = (z_f - z_i)$$

$$w = -(0.120\text{ kg}) \times (9.81\text{ m s}^{-2}) \times (50\text{ m}) = -59\text{ J} = \boxed{59\text{ J needed}}$$

E2.2(b) This is an expansion against a constant external pressure, hence $w = -p_{ex}\Delta V$. [2.8]

The change in volume is the cross-sectional area times the linear displacement:

$$\Delta V = (50.0\text{ cm}^2) \times (15\text{ cm}) \times \left(\frac{1\text{ m}}{100\text{ cm}}\right)^3 = 7.5 \times 10^{-4}\text{ m}^3$$

so $w = -(121 \times 10^3\text{ Pa}) \times (7.5 \times 10^{-4}\text{ m}^3) = \boxed{-91\text{ J}}$ as $1\text{ Pa m}^3 = 1\text{ J}$

E2.3(b) For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. (See Section 2.2a and Section 2.11(b) for a more complete discussion.) From the definition of enthalpy, $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$ (perfect gas). Hence, $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas.

(a) $\boxed{\Delta U = \Delta H = 0}$

$$w = -nRT\ln\left(\frac{V_f}{V_i}\right) [2.10]$$

$$= -(2.00\text{ mol}) \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (22 + 273)\text{ K} \times \ln\frac{31.7\text{ dm}^3}{22.8\text{ dm}^3} = \boxed{-1.62 \times 10^3\text{ J}}$$

$$q = -w = \boxed{1.62 \times 10^3\text{ J}}$$

(b) $\boxed{\Delta U = \Delta H = 0}$

$$w = -p_{ex}\Delta V [2.8]$$

where p_{ex} in this case can be computed from the perfect gas law

$$pV = nRT$$

so $p = \dfrac{(2.00\text{ mol}) \times (8.3145\text{ JK}^{-1}\text{ mol}^{-1}) \times (22 + 273)\text{ K}}{31.7\text{ dm}^3} \times (10\text{ dm m}^{-1})^3 = 1.55 \times 10^5\text{ Pa}$

and $w = \dfrac{-(1.55 \times 10^5\text{ Pa}) \times (31.7 - 22.8)\text{ dm}^3}{(10\text{ dm m}^{-1})^3} = \boxed{-1.38 \times 10^3\text{ J}}$

$$q = -w = \boxed{1.38 \times 10^3\text{ J}}$$

(c) $\boxed{\Delta U = \Delta H = 0}$

$\boxed{w = 0}$ [free expansion] $\quad q = \Delta U - w = 0 - 0 = \boxed{0}$

COMMENT. An isothermal free expansion of a perfect gas is also adiabatic.

E2.4(b) The perfect gas law leads to

$$\frac{p_1V}{p_2V}=\frac{nRT_1}{nRT_2}, \quad \text{or} \quad p_2=\frac{p_1T_2}{T_1}=\frac{(111\text{ k Pa})\times(356\text{ K})}{277\text{ K}}=\boxed{143\text{ k Pa}}$$

There is no change in volume, so $\boxed{w=0}$. The heat flow is

$$q=\int C_V\,\mathrm{d}T\approx C_V\Delta T=(2.5)\times(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(2.00\text{ mol})\times(356-277)\text{ K}$$

$$=\boxed{3.28\times10^3\text{ J}}$$

$$\Delta U=q+w=\boxed{3.28\times10^3\text{ J}}$$

E2.5(b) (a) $w=-p_{\text{ex}}\Delta V=\dfrac{-(7.7\times10^3\text{ Pa})\times(2.5\text{ dm}^3)}{(10\text{ dm m}^{-1})^3}=\boxed{-19\text{ J}}$

(b) $w=-nRT\ln\left(\dfrac{V_f}{V_i}\right)$ [2.10]

$$w=-\left(\frac{6.56\text{ g}}{39.95\text{ g mol}^{-1}}\right)\times(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(305\text{ K})\times\ln\frac{(2.5+18.5)\text{dm}^3}{18.5\text{ dm}^3}$$

$$=\boxed{-52.8\text{ J}}$$

E2.6(b) $\Delta H=\Delta_{\text{cond}}H=-\Delta_{\text{vap}}H=-(2.00\text{ mol})\times(35.3\text{ kJ mol}^{-1})=\boxed{-70.6\text{ kJ}}$

Since the condensation is done isothermally and reversibly, the external pressure is constant at 1.00 atm. Hence,

$$q=q_p=\Delta H=\boxed{-70.6\text{ kJ}}$$

$w=-p_{\text{ex}}\Delta V$ [2.8], where $\Delta V=V_{\text{liq}}-V_{\text{vap}}\approx-V_{\text{vap}}$ because $V_{\text{liq}}\ll V_{\text{vap}}$

On the assumption that methanol vapour is a perfect gas, $V_{\text{vap}}=\dfrac{nRT}{p}$ and $p=p_{\text{ex}}$, since the condensation is done reversibly. Hence,

$$w\approx nRT=(2.00\text{ mol})\times(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(64+273)\text{ K}=\boxed{5.60\times10^3\text{ J}}$$

and $\Delta U=q+w=(-70.6+5.60)\text{ kJ}=\boxed{-65.0\text{ kJ}}$

E2.7(b) The reaction is

$$\text{Zn}+2\,\text{H}^+\rightarrow\text{Zn}^{2+}+\text{H}_2$$

so it liberates 1 mol of $H_2(g)$ for every 1 mol Zn used. Work at constant pressure is

$$w=-p_{\text{ex}}\Delta V=-pV_{\text{gas}}=-nRT$$

$$=-\left(\frac{5.0\text{ g}}{65.4\text{ g mol}^{-1}}\right)\times(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(23+273)\text{ K}=\boxed{-188\text{ J}}$$

E2.8(b) (a) At constant pressure, $q = \Delta H$.

$$q = \int C_p \mathrm{d}T = \int_{0+273\,\mathrm{K}}^{100+273\,\mathrm{K}} [20.17 + (0.4001)T/\mathrm{K}]\,\mathrm{d}T \text{ J K}^{-1}$$

$$= \left[(20.17)T + \frac{1}{2}(0.4001) \times \left(\frac{T^2}{\mathrm{K}}\right)\right]\Bigg|_{273\,\mathrm{K}}^{373\,\mathrm{K}} \text{ J K}^{-1}$$

$$= [(20.17) \times (373 - 273) + \tfrac{1}{2}(0.4001) \times (373^2 - 273^2)]\text{J} = \boxed{14.9 \times 10^3\,\text{J}} = \Delta H$$

$$w = -p\Delta V = -nR\Delta T = -(1.00\text{ mol}) \times (8.3145\text{ J K}^{-1}\text{mol}^{-1}) \times (100\text{ K}) = \boxed{-831\text{ J}}$$

$$\Delta U = q + w = (14.9 - 0.831)\text{ kJ} = \boxed{14.1\text{ kJ}}$$

(b) The energy and enthalpy of a perfect gas depend on temperature alone. Thus, $\Delta H = \boxed{14.9\text{ kJ}}$ and $\Delta U = \boxed{14.1\text{ kJ}}$, as above. At constant volume, $w = \boxed{0}$ and $\Delta U = q$, so $q = \boxed{+14.1\text{ kJ}}$.

E2.9(b) For reversible adiabatic expansion

$$T_\mathrm{f} = T_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{1/c} \text{ [2.28a]}$$

where $c = \dfrac{C_{V,\mathrm{m}}}{R} = \dfrac{C_{p,\mathrm{m}} - R}{R} = \dfrac{(37.11 - 8.3145)\text{ J K}^{-1}\text{mol}^{-1}}{8.3145\text{ J K}^{-1}\text{mol}^{-1}} = 3.463$

therefore, the final temperature is

$$T_\mathrm{f} = (298.15\text{ K}) \times \left(\frac{500 \times 10^{-3}\text{ dm}^3}{2.00\text{ dm}^3}\right)^{1/3.463} = \boxed{200\text{ K}}$$

E2.10(b) Reversible adiabatic work is

$$w = C_V\Delta T\,[2.27] = n(C_{p,\mathrm{m}} - R) \times (T_\mathrm{f} - T_\mathrm{i})$$

where the temperatures are related by

$$T_\mathrm{f} = T_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{1/c} \text{ [2.28a], where } c = \frac{C_{V,\mathrm{m}}}{R} = \frac{C_{p,\mathrm{m}} - R}{R} = 2.503$$

So $T_\mathrm{f} = [(23.0 + 273.15)\mathrm{K}] \times \left(\dfrac{400 \times 10^{-3}\text{ dm}^3}{2.00\text{ dm}^3}\right)^{1/2.503} = 156\text{ K}$

and $w = \left(\dfrac{3.12\text{ g}}{28.0\text{ g mol}^{-1}}\right) \times (29.125 - 8.3145)\text{ J K}^{-1}\text{mol}^{-1} \times (156 - 296)\mathrm{K} = \boxed{-325\text{ J}}$

E2.11(b) For reversible adiabatic expansion

$$p_\mathrm{f}V_\mathrm{f}^\gamma = p_\mathrm{i}V_\mathrm{i}^\gamma \text{ [2.29], so } p_\mathrm{f} = p_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^\gamma = (87.3\text{ Torr}) \times \left(\frac{500 \times 10^{-3}\text{ dm}^3}{3.0\text{ dm}^3}\right)^{1.3} = \boxed{8.5\text{ Torr}}$$

E2.12(b) $q_p = nC_{p,\mathrm{m}}\Delta T\,[2.24]$

$$C_{p,\mathrm{m}} = \frac{q_p}{n\Delta T} = \frac{178\ \mathrm{J}}{1.9\ \mathrm{mol} \times 1.78\ \mathrm{K}} = \boxed{53\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

$$C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R = (53 - 8.3)\ \mathrm{J\ K^{-1}\ mol^{-1}} = \boxed{45\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

E2.13(b) $\Delta H = q_p = C_p\Delta T\ [2.23\mathrm{b}, 2.24] = nC_{p,\mathrm{m}}\Delta T$

$$\Delta H = q_p = (2.0\ \mathrm{mol}) \times (37.11\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (277 - 250)\ \mathrm{K} = \boxed{2.0 \times 10^3\ \mathrm{J\ mol^{-1}}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T \quad \text{so} \quad \Delta U = \Delta H - nR\Delta T$$

$$\Delta U = 2.0 \times 10^3\ \mathrm{J\ mol^{-1}} - (2.0\ \mathrm{mol}) \times (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (277 - 250)\ \mathrm{K}$$
$$= \boxed{1.6 \times 10^3\ \mathrm{J\ mol^{-1}}}$$

E2.14(b) In an adiabatic process, $q = \boxed{0}$. Work against a constant external pressure is

$$w = -p_{\mathrm{ex}}\Delta V = \frac{-(78.5 \times 10^3\ \mathrm{Pa}) \times (4 \times 15 - 15)\ \mathrm{dm^3}}{(10\ \mathrm{dm\ m^{-1}})^3} = \boxed{-3.5 \times 10^3\ \mathrm{J}}$$

$$\Delta U = q + w = \boxed{-3.5 \times 10^3\ \mathrm{J}}$$

One can also relate adiabatic work to ΔT (eqn 2.27):

$$w = C_V\Delta T = n(C_{p,\mathrm{m}} - R)\Delta T, \quad \text{so} \quad \Delta T = \frac{w}{n(C_{p,\mathrm{m}} - R)}$$

$$\Delta T = \frac{-3.5 \times 10^3\ \mathrm{J}}{(5.0\ \mathrm{mol}) \times (37.11 - 8.3145)\ \mathrm{J\ K^{-1}\ mol^{-1}}} = \boxed{-24\ \mathrm{K}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$
$$= -3.5 \times 10^3\ \mathrm{J} + (5.0\ \mathrm{mol}) \times (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (-24\ \mathrm{K}) = \boxed{-4.5 \times 10^3\ \mathrm{J}}$$

E2.15(b) In an adiabatic process, the initial and final pressures are related by (eqn 2.29):

$$p_{\mathrm{f}}V_{\mathrm{f}}^{\gamma} = p_{\mathrm{i}}V_{\mathrm{i}}^{\gamma}, \quad \text{where} \quad \gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{C_{p,\mathrm{m}}}{C_{p,\mathrm{m}} - R} = \frac{20.8\ \mathrm{J\ K^{-1}\ mol^{-1}}}{(20.8 - 8.31)\ \mathrm{J\ K^{-1}\ mol^{-1}}} = 1.67$$

Find V_{i} from the perfect gas law:

$$V_{\mathrm{i}} = \frac{nRT_{\mathrm{i}}}{p_{\mathrm{i}}} = \frac{(1.5\ \mathrm{mol})(8.31\ \mathrm{J\ K^{-1}\ mol^{-1}})(315\ \mathrm{K})}{230 \times 10^3\ \mathrm{Pa}} = 0.017\overline{1}\ \mathrm{m^3}$$

$$\text{so} \quad V_{\mathrm{f}} = V_{\mathrm{i}}\left(\frac{p_{\mathrm{i}}}{p_{\mathrm{f}}}\right)^{1/\gamma} = (0.017\overline{1}\ \mathrm{m^3})\left(\frac{230\ \mathrm{kPa}}{170\ \mathrm{kPa}}\right)^{1/1.67} = \boxed{0.020\overline{5}\ \mathrm{m^3}}$$

Find the final temperature from the perfect gas law:

$$T_{\mathrm{f}} = \frac{p_{\mathrm{f}}V_{\mathrm{f}}}{nR} = \frac{(170 \times 10^3\ \mathrm{Pa}) \times (0.020\overline{5}\ \mathrm{m^3})}{(1.5\ \mathrm{mol})(8.31\ \mathrm{J\ K^{-1}\ mol^{-1}})} = \boxed{27\overline{9}\ \mathrm{K}}$$

Adiabatic work is (eqn 2.27)

$$w = C_V\Delta T = (20.8 - 8.31)\ \text{J K}^{-1}\,\text{mol}^{-1} \times 1.5\ \text{mol} \times (27\overline{9} - 315)\ \text{K} = \boxed{-6.\overline{7}\times 10^2\ \text{J}}$$

E2.16(b) At constant pressure

$$q = \Delta H = n\Delta_{\text{vap}}H^{\circ} = (0.75\ \text{mol}) \times (32.0\ \text{kJ mol}^{-1}) = \boxed{24.\overline{0}\ \text{kJ}}$$

and $w = -p\Delta V \approx -pV_{\text{vapor}} = -nRT = -(0.75\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (260\ \text{K})$

$$w = -1.6 \times 10^3\ \text{J} = \boxed{-1.6\ \text{kJ}}$$

$$\Delta U = w + q = 24.\overline{0} - 1.6\ \text{kJ} = \boxed{22.\overline{4}\ \text{kJ}}$$

COMMENT. Because the vapour is here treated as a perfect gas, the specific value of the external pressure provided in the statement of the exercise does not affect the numerical value of the answer.

E2.17(b) The lattice enthalpy is the difference in enthalpy between an ionic solid and the corresponding isolated ions. In this exercise, it is the enthalpy corresponding to the process

$$\text{MgBr}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{Br}^-(\text{g})$$

The standard lattice enthalpy can be computed from the standard enthalpies given in the exercise by considering the formation of $\text{MgBr}_2(\text{s})$ from its elements as occurring through the following steps: sublimation of Mg(s), removing two electrons from Mg(g), vaporization of $\text{Br}_2(\text{l})$, atomization of $\text{Br}_2(\text{g})$, electron attachment to Br(g), and formation of the solid MgBr_2 lattice from gaseous ions:

$$\begin{aligned}\Delta_f H^{\circ}(\text{MgBr}_2,\text{s}) = {} & \Delta_{\text{sub}}H^{\circ}(\text{Mg},\text{s}) + \Delta_{\text{ion}}H^{\circ}(\text{Mg},\text{g}) + \Delta_{\text{vap}}H^{\circ}(\text{Br}_2,\text{l}) \\ & + \Delta_{\text{at}}H^{\circ}(\text{Br}_2,\text{g}) + 2\Delta_{\text{eg}}H^{\circ}(\text{Br},\text{g}) - \Delta_{\text{L}}H^{\circ}(\text{MgBr}_2,\text{s})\end{aligned}$$

So, the lattice enthalpy is

$$\begin{aligned}\Delta_{\text{L}}H^{\circ}(\text{MgBr}_2,\text{s}) = {} & \Delta_{\text{sub}}H^{\circ}(\text{Mg},\text{s}) + \Delta_{\text{ion}}H^{\circ}(\text{Mg},\text{g}) + \Delta_{\text{vap}}H^{\circ}(\text{Br}_2,\text{l}) \\ & + \Delta_{\text{at}}H^{\circ}(\text{Br}_2,\text{g}) + 2\Delta_{\text{eg}}H^{\circ}(\text{Br},\text{g}) - \Delta_f H^{\circ}(\text{MgBr}_2,\text{s})\end{aligned}$$

$$\Delta_{\text{L}}H^{\circ}(\text{MgBr}_2,\text{s}) = [148 + 2187 + 31 + 193 - 2(331) + 524]\ \text{kJ mol}^{-1} = \boxed{2421\ \text{kJ mol}^{-1}}$$

E2.18(b) The reaction is

$$\text{C}_6\text{H}_5\text{OH}(\text{l}) + 7\,\text{O}_2(\text{g}) \rightarrow 6\,\text{CO}_2(\text{g}) + 3\,\text{H}_2\text{O}(\text{l})$$

$$\begin{aligned}\Delta_c H^{\circ} &= 6\Delta_f H^{\circ}(\text{CO}_2) + 3\Delta_f H^{\circ}(\text{H}_2\text{O}) - \Delta_f H^{\circ}(\text{C}_6\text{H}_5\text{OH}) - 7\Delta_f H^{\circ}(\text{O}_2) \\ &= [6(-393.51) + 3(-285.83) - (-165.0) - 7(0)]\ \text{kJ mol}^{-1} = \boxed{-3053.6\ \text{kJ mol}^{-1}}\end{aligned}$$

E2.19(b) We need $\Delta_f H^{\circ}$ for the reaction

(4) $2\,\text{B}(\text{s}) + 3\,\text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g})$

reaction (4) = reaction (2) + 3 × reaction (3) – reaction (1)

Thus, $\Delta_f H^{\circ} = \Delta_r H^{\circ}\{\text{reaction(2)}\} + 3 \times \Delta_r H^{\circ}\{\text{reaction(3)}\} - \Delta_r H^{\circ}\{\text{reaction(1)}\}$

$$= [-1274 + 3 \times (-241.8) - (-2036)]\ \text{kJ mol}^{-1} = \boxed{+36.6\ \text{kJ mol}^{-1}}$$

E2.20(b) For anthracene the reaction is

$$C_{14}H_{10}(s) + \tfrac{33}{2}O_2(g) \rightarrow 14\,CO_2(g) + 5\,H_2O(l)$$

$$\Delta_c U^\circ = \Delta_c H^\circ - \Delta n_g RT\ [2.21], \quad \Delta n_g = -\tfrac{5}{2}\text{ mol}$$

$$\Delta_c U^\circ = -7061\text{ kJ mol}^{-1} - (-\tfrac{5}{2} \times 8.3 \times 10^{-3}\text{ kJ K}^{-1}\text{mol}^{-1} \times 298\text{ K})$$
$$= -7055\text{ kJ mol}^{-1}$$

$$|q| = |q_V| = |n\Delta_c U^\circ| = \left(\frac{2.25 \times 10^{-3}\text{ g}}{178.23\text{ g mol}^{-1}}\right) \times (7055\text{ kJ mol}^{-1}) = 0.0891\text{ kJ}$$

$$C = \frac{|q|}{\Delta T} = \frac{0.0891\text{ kJ}}{1.35\text{ K}} = 0.0660\text{ kJ K}^{-1} = \boxed{66.0\text{ J K}^{-1}}$$

When phenol is used the reaction is $C_6H_5OH(s) + \tfrac{15}{2}O_2(g) \rightarrow 6\,CO_2(g) + 3\,H_2O(l)$

$$\Delta_c H^\circ = -3054\text{ kJ mol}^{-1}\ [\text{Table 2.6}]$$

$$\Delta_c U^\circ = \Delta_c H^\circ - \Delta n_g RT,\ \Delta n_g = -\tfrac{3}{2}$$
$$= (-3054\text{ kJ mol}^{-1}) + (\tfrac{3}{2}) \times (8.314 \times 10^{-3}\text{ kJ K}^{-1}\text{mol}^{-1}) \times (298\text{ K})$$
$$= -3050\text{ kJ mol}^{-1}$$

$$|q| = \left(\frac{135 \times 10^{-3}\text{ g}}{94.12\text{ g mol}^{-1}}\right) \times (3050\text{ kJ mol}^{-1}) = 4.37\bar{5}\text{ kJ}$$

$$\Delta T = \frac{|q|}{C} = \frac{4.37\bar{5}\text{ kJ}}{0.0660\text{ kJ K}^{-1}} = \boxed{+66.3\text{ K}}$$

COMMENT. In this case $\Delta_c U^\circ$ and $\Delta_c H^\circ$ differed by about 0.1%. Thus, to within 3 significant figures, it would not have mattered if we had used $\Delta_c H^\circ$ instead of $\Delta_c U^\circ$, but for very precise work it would.

E2.21(b) The reaction is $AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$

$$\Delta_{sol} H^\circ = \Delta_f H^\circ(Ag^+,aq) + \Delta_f H^\circ(Br^-,aq) - \Delta_f H^\circ(AgBr,s)$$
$$= [105.58 + (-121.55) - (-100.37)]\text{ kJ mol}^{-1} = \boxed{+84.40\text{ kJ mol}^{-1}}$$

E2.22(b) The combustion products of graphite and diamond are the same, so the transition $C(gr) \rightarrow C(d)$ is equivalent to the combustion of graphite plus the reverse of the combustion of diamond, and

$$\Delta_{trans} H^\circ = [-393.51 - (-395.41)]\text{ kJ mol}^{-1} = \boxed{+1.90\text{ kJ mol}^{-1}}$$

E2.23(b) (a) reaction(3) = (−2) × reaction(1) + reaction(2) and $\Delta n_g = -1$

The enthalpies of reactions are combined in the same manner as the equations (Hess's law).

$$\Delta_r H^\circ(3) = (-2) \times \Delta_r H^\circ(1) + \Delta_r H^\circ(2)$$
$$= [(-2) \times (52.96) + (-483.64)]\text{ kJ mol}^{-1} = \boxed{-589.56\text{ kJ mol}^{-1}}$$

$$\Delta_r U^\circ = \Delta_r H^\circ - \Delta n_g RT = -589.56\text{ kJ mol}^{-1} - (-3) \times (8.314\text{ J K}^{-1}\text{mol}^{-1}) \times (298\text{ K})$$
$$= -589.56\text{ kJ mol}^{-1} + 7.43\text{ kJ mol}^{-1} = \boxed{-582.13\text{ kJ mol}^{-1}}$$

(b) $\Delta_r H^\ominus$ refers to the formation of one mole of the compound, so

$$\Delta_f H^\ominus(\mathrm{HI}) = \tfrac{1}{2}(52.96\ \mathrm{kJ\ mol^{-1}}) = \boxed{26.48\ \mathrm{kJ\ mol^{-1}}}$$

$$\Delta_f H^\ominus(\mathrm{H_2O}) = \tfrac{1}{2}(-483.64\ \mathrm{kJ\ mol^{-1}}) = \boxed{-241.82\ \mathrm{kJ\ mol^{-1}}}$$

E2.24(b) $\Delta_r H^\ominus = \Delta_r U^\ominus + RT\Delta n_g$ [2.21]

$$= -772.7\ \mathrm{kJ\ mol^{-1}} + (5)\times(8.3145\times10^{-3}\ \mathrm{kJ\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})$$

$$= \boxed{-760.3\ \mathrm{kJ\ mol^{-1}}}$$

E2.25(b) Combine the reactions in such a way that the combination is the desired formation reaction. The enthalpies of the reactions are then combined in the same way as the equations to yield the enthalpy of formation.

	$\Delta_r H^\ominus/(\mathrm{kJ\ mol^{-1}})$
$\tfrac{1}{2}\mathrm{N_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{NO(g)}$	$+90.25$
$\mathrm{NO(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NOCl(g)}$	$-\tfrac{1}{2}(75.5)$
$\tfrac{1}{2}\mathrm{N_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NOCl(g)}$	$+52.5$

Hence, $\Delta_f H^\ominus(\mathrm{NOCl, g}) = \boxed{+52.5\ \mathrm{kJ\ mol^{-1}}}$

E2.26(b) According to Kirchhoff's law [2.36a]

$$\Delta_r H^\ominus(100°\mathrm{C}) = \Delta_r H^\ominus(25°\mathrm{C}) + \int_{25°\mathrm{C}}^{100°\mathrm{C}} \Delta_r C_p^\ominus \mathrm{d}T$$

where Δ_r as usual signifies a sum over product and reactant species weighted by stoichiometric coefficients. Because $C_{p,\mathrm{m}}$ can frequently be parametrized as

$$C_{p,\mathrm{m}} = a + bT + c/T^2$$

the indefinite integral of $C_{p,\mathrm{m}}$ has the form

$$\int C_{p,\mathrm{m}}\mathrm{d}T = aT + \tfrac{1}{2}bT^2 - c/T$$

Combining this expression with our original integral, we have

$$\Delta_r H^\ominus(100°\mathrm{C}) = \Delta_r H^\ominus(25°\mathrm{C}) + (T\Delta_r a + \tfrac{1}{2}T^2\Delta_r b - \Delta_r c/T)\Big|_{298\ \mathrm{K}}^{373\ \mathrm{K}}$$

Now, for the pieces

$$\Delta_r H^\ominus(25°\mathrm{C}) = 2(-285.83\ \mathrm{kJ\ mol^{-1}}) - 2(0) - 0 = -571.66\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r a = [2(75.29) - 2(27.28) - (29.96)]\ \mathrm{J\ K^{-1}\ mol^{-1}} = 0.06606\ \mathrm{kJ\ K^{-1}\ mol^{-1}}$$

$$\Delta_r b = [2(0) - 2(3.29) - (4.18)]\times10^{-3}\ \mathrm{J\ K^{-2}\ mol^{-1}} = -10.76\times10^{-6}\ \mathrm{kJ\ K^{-2}\ mol^{-1}}$$

$$\Delta_r c = [2(0) - 2(0.50) - (-1.67)]\times10^{5}\ \mathrm{J\ K\ mol^{-1}} = 67\ \mathrm{kJ\ K\ mol^{-1}}$$

$$\begin{aligned}\Delta_r H^\ominus(100^\circ\text{C}) &= [-571.66 + (373-298)\times(0.06606) + \tfrac{1}{2}(373^2-298^2) \\ &\quad \times(-10.76\times10^{-6}) - (67)\times(\tfrac{1}{373}-\tfrac{1}{298})]\ \text{kJ mol}^{-1} \\ &= \boxed{-566.93\ \text{kJ mol}^{-1}}\end{aligned}$$

E2.27(b) The hydrogenation reaction is

$$(1)\ \text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) \quad \Delta_r H^\ominus(T) = ?$$

The reactions and accompanying data which are to be combined in order to yield reaction (1) and $\Delta_r H^\ominus(T)$ are

$$(2)\ \text{H}_2(\text{g}) + \tfrac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)} \quad \Delta_c H^\ominus(2) = -285.83\ \text{kJ mol}^{-1}$$

$$(3)\ \text{C}_2\text{H}_4(\text{g}) + 3\,\text{O}_2(\text{g}) \rightarrow 2\,\text{H}_2\text{O(l)} + 2\,\text{CO}_2(\text{g}) \quad \Delta_c H^\ominus(3) = -1411\ \text{kJ mol}^{-1}$$

$$(4)\ \text{C}_2\text{H}_2(\text{g}) + \tfrac{5}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)} + 2\,\text{CO}_2(\text{g}) \quad \Delta_c H^\ominus(4) = -1300\ \text{kJ mol}^{-1}$$

reaction (1) = reaction (2) − reaction (3) + reaction (4)

Hence, at 298 K:

(a)
$$\begin{aligned}\Delta_r H^\ominus &= \Delta_c H^\ominus(2) - \Delta_c H^\ominus(3) + \Delta_c H^\ominus(4) \\ &= [(-285.83) - (-1411) + (-1300)]\ \text{kJ mol}^{-1} \\ &= \boxed{-175\ \text{kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT\ [2.21]; \quad \Delta n_g = -1 \\ &= -175\ \text{kJ mol}^{-1} - (-1)\times(2.48\ \text{kJ mol}^{-1}) \\ &= \boxed{-173\ \text{kJ mol}^{-1}}\end{aligned}$$

(b) At 348 K:

$$\Delta_r H^\ominus(348\ \text{K}) = \Delta_r H^\ominus(298\ \text{K}) + \Delta_r C_p^\ominus(348\ \text{K} - 298\ \text{K}) \quad [\text{Example 2.6}]$$

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_J \nu_J C_{p,\text{m}}^\ominus(\text{J})\,[2.36\text{b}] = C_{p,\text{m}}^\ominus(\text{C}_2\text{H}_4,\text{g}) - C_{p,\text{m}}^\ominus(\text{C}_2\text{H}_2,\text{g}) - C_{p,\text{m}}^\ominus(\text{H}_2,\text{g}) \\ &= (43.56 - 43.93 - 28.82)\times10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1} \\ &= -29.19\times10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus(348\,\text{K}) &= (-175\ \text{kJ mol}^{-1}) - (29.19\times10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\times(50\ \text{K}) \\ &= \boxed{-176\ \text{kJ mol}^{-1}}\end{aligned}$$

E2.28(b) NaCl, AgNO_3, and NaNO_3 are strong electrolytes, therefore the net ionic equation is

$$\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl(s)}$$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(\text{AgCl}) - \Delta_f H^\ominus(\text{Ag}^+) - \Delta_f H^\ominus(\text{Cl}^-) \\ &= [(-127.07) - (105.58) - (-167.16)]\ \text{kJ mol}^{-1} \\ &= \boxed{-65.49\ \text{kJ mol}^{-1}}\end{aligned}$$

2.29(b) The cycle is shown in Figure 2.1.

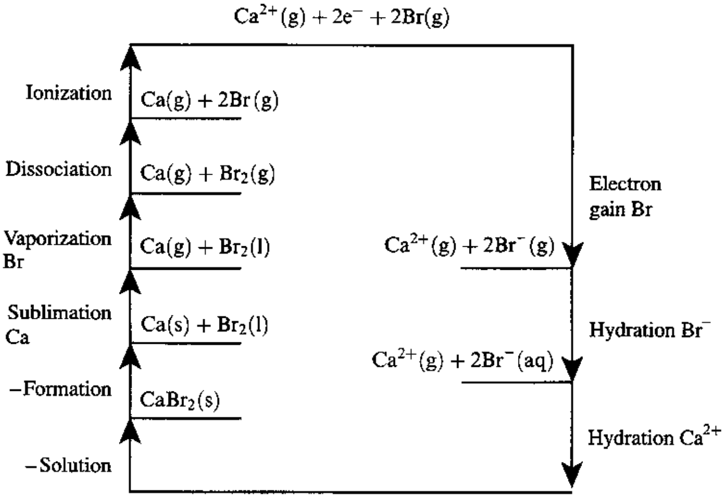


Figure 2.1

$$\begin{aligned}-\Delta_{\text{hyd}}H^{\ominus}(Ca^{2+}) &= -\Delta_{\text{soln}}H^{\ominus}(CaBr_2) - \Delta_f H^{\ominus}(CaBr_2,s) + \Delta_{\text{sub}}H^{\ominus}(Ca)\\ &\quad + \Delta_{\text{vap}}H^{\ominus}(Br_2) + \Delta_{\text{diss}}H^{\ominus}(Br_2) + \Delta_{\text{ion}}H^{\ominus}(Ca)\\ &\quad + \Delta_{\text{ion}}H^{\ominus}(Ca^+) + 2\Delta_{\text{eg}}H^{\ominus}(Br) + 2\Delta_{\text{hyd}}H^{\ominus}(Br^-)\\ &= [-(-103.1) - (-682.8) + 178.2 + 30.91 + 192.9\\ &\quad + 589.7 + 1145 + 2(-331.0) + 2(97.5)]\text{ kJ mol}^{-1}\\ &= \boxed{2456\text{ kJ mol}^{-1}}\end{aligned}$$

so $\Delta_{\text{hyd}}H^{\ominus}(Ca^{2+}) = \boxed{-2456\text{ kJ mol}^{-1}}$

2.30(b) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-10\text{ K}}{(1.00 - 22)\text{ atm}} = \boxed{0.48\text{ K atm}^{-1}}$$

2.31(b) The internal energy is a function of temperature and volume, $U_m = U_m(T, V_m)$, so

$$dU_m = \left(\frac{\partial U_m}{\partial T}\right)_{V_m} dT + \left(\frac{\partial U_m}{\partial V_m}\right)_T dV_m \quad [\pi_T = (\partial U_m/\partial V)_T]$$

For an isothermal expansion $dT = 0$, hence

$$dU_m = \left(\frac{\partial U_m}{\partial V_m}\right)_T dV_m = \pi_T\, dV_m = \frac{a}{V_m^2}dV_m$$

$$\Delta U_m = \int_{V_{m,1}}^{V_{m,2}} dU_m = \int_{V_{m,1}}^{V_{m,2}} \frac{a}{V_m^2}dV_m = a\int_{1.00\text{ dm}^3\text{ mol}^{-1}}^{22.1\text{ dm}^3\text{ mol}^{-1}} \frac{dV_m}{V_m^2} = -\frac{a}{V_m}\Bigg|_{1.00\text{ dm}^3\text{ mol}^{-1}}^{22.1\text{ dm}^3\text{ mol}^{-1}}$$

$$= -\frac{a}{22.1\text{ dm}^3\text{ mol}^{-1}} + \frac{a}{1.00\text{ dm}^3\text{ mol}^{-1}} = \frac{21.1a}{22.1\text{ dm}^3\text{ mol}^{-1}} = 0.954\overline{75}a\text{ dm}^{-3}\text{ mol}$$

From Table 1.6, $a = 1.337\ \mathrm{dm^6\ atm\ mol^{-2}}$

$$\Delta U_\mathrm{m} = (0.95475\ \mathrm{mol\ dm^3}) \times (1.337\ \mathrm{atm\ dm^6\ mol^{-2}})$$

$$= (1.27\overline{65}\ \mathrm{atm\ dm^3\ mol^{-1}}) \times (1.01325 \times 10^5\ \mathrm{Pa\ atm^{-1}}) \times \left(\frac{1\ \mathrm{m^3}}{10^3\ \mathrm{dm^3}}\right)$$

$$= 129\ \mathrm{Pa\ m^3\ mol^{-1}} = \boxed{129\ \mathrm{J\ mol^{-1}}}$$

$$w = -\int p\,\mathrm{d}V_\mathrm{m}, \quad \text{where} \quad p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2} \text{ for a van der Waals gas. Hence,}$$

$$w = -\int \left(\frac{RT}{V_\mathrm{m} - b}\right)\mathrm{d}V_\mathrm{m} + \int \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m} = -q + \Delta U_\mathrm{m}$$

Thus,

$$q = \int_{1.00\ \mathrm{dm^3\ mol^{-1}}}^{22.1\ \mathrm{dm^3\ mol^{-1}}} \left(\frac{RT}{V_m - b}\right) dV_\mathrm{m} = RT\ln(V_\mathrm{m} - b)\Big|_{1.00\ \mathrm{dm^3\ mol^{-1}}}^{22.1\ \mathrm{dm^3\ mol^{-1}}}$$

$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K}) \times \ln\left(\frac{22.1 - 3.20 \times 10^{-2}}{1.00 - 3.20 \times 10^{-2}}\right) = \boxed{+7.74\overline{65}\ \mathrm{kJ\ mol^{-1}}}$$

and $w = -q + \Delta U_\mathrm{m} = -(774\overline{7}\ \mathrm{J\ mol^{-1}}) + (129\ \mathrm{J\ mol^{-1}}) = \boxed{-761\overline{8}\ \mathrm{J\ mol^{-1}}} = \boxed{-7.62\ \mathrm{kJ\ mol^{-1}}}$

E2.32(b) The expansion coefficient is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{V'(3.7 \times 10^{-4}\,\mathrm{K^{-1}} + 2 \times 1.52 \times 10^{-6}T\ \mathrm{K^{-2}})}{V}$$

$$= \frac{V'[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6}(T/\mathrm{K})]\ \mathrm{K^{-1}}}{V'[0.77 + 3.7 \times 10^{-4}(T/\mathrm{K}) + 1.52 \times 10^{-6}(T/\mathrm{K})^2]}$$

$$= \frac{[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6}(310)]\ \mathrm{K^{-1}}}{0.77 + 3.7 \times 10^{-4}(310) + 1.52 \times 10^{-6}(310)^2} = \boxed{1.27 \times 10^{-3}\ \mathrm{K^{-1}}}$$

E2.33(b) Isothermal compressibility is

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \approx -\frac{\Delta V}{V\Delta p} \quad \text{so} \quad \Delta p = -\frac{\Delta V}{V\kappa_T}$$

A density increase of 0.08% means $\Delta V/V = -0.0008$. So, the additional pressure that must be applied is

$$\Delta p = \frac{0.0008}{2.21 \times 10^{-6}\ \mathrm{atm^{-1}}} = \boxed{3.\overline{6} \times 10^2\ \mathrm{atm}}$$

E2.34(b) The isothermal Joule–Thomson coefficient is

$$\left(\frac{\partial H_\mathrm{m}}{\partial p}\right)_T = -\mu C_{p,\mathrm{m}} = -(1.11\ \mathrm{K\ atm^{-1}}) \times (37.11\ \mathrm{J\ K^{-1}\ mol^{-1}}) = \boxed{-41.2\ \mathrm{J\ atm^{-1}\ mol^{-1}}}$$

If this coefficient is constant in an isothermal Joule–Thomson experiment, then the heat that must be supplied to maintain constant temperature is ΔH in the following relationship

$$\frac{\Delta H/n}{\Delta p} = -41.2\ \mathrm{J\ atm^{-1}\ mol^{-1}} \quad \text{so} \quad \Delta H = -(41.2\ \mathrm{J\ atm^{-1}\ mol^{-1}})n\Delta p$$

$$\Delta H = -(41.2\ \mathrm{J\ atm^{-1}\ mol^{-1}}) \times (12.0\ \mathrm{mol}) \times (-55\ \mathrm{atm}) = \boxed{27.\bar{2} \times 10^3\ \mathrm{J}}$$

Solutions to problems

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298 K.

Solutions to numerical problems

P2.2

$$w = -p_{\mathrm{ex}}\Delta V\ [2.8] \quad V_{\mathrm{f}} = \frac{nRT}{p_{\mathrm{ex}}} \gg V_{\mathrm{i}}; \quad \text{so} \quad \Delta V \approx V_{\mathrm{f}}$$

Hence, $w \approx (-p_{\mathrm{ex}}) \times \left(\dfrac{nRT}{p_{\mathrm{ex}}}\right) = -nRT = (-1.0\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (1073\ \mathrm{K})$

$$w \approx \boxed{-8.9\ \mathrm{kJ}}$$

Even if there is no physical piston, the gas drives back the atmosphere, so the work is also

$$w \approx \boxed{-8.9\ \mathrm{kJ}}$$

P2.4 The virial expression for pressure up to the second coefficient is

$$p = \left(\frac{RT}{V_{\mathrm{m}}}\right)\left(1 + \frac{B}{V_{\mathrm{m}}}\right)\ [1.19\mathrm{b}]$$

$$w = -\int_{\mathrm{i}}^{\mathrm{f}} p\,\mathrm{d}V = -n\int_{\mathrm{i}}^{\mathrm{f}} \left(\frac{RT}{V_{\mathrm{m}}}\right) \times \left(1 + \frac{B}{V_{\mathrm{m}}}\right)\mathrm{d}V_{\mathrm{m}} = -nRT\ln\left(\frac{V_{\mathrm{m,f}}}{V_{\mathrm{m,i}}}\right) + nBRT\left(\frac{1}{V_{\mathrm{m,f}}} - \frac{1}{V_{\mathrm{m,i}}}\right)$$

From the data,

$$nRT = (70 \times 10^{-3}\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (373\ \mathrm{K}) = 21\bar{7}\ \mathrm{J}$$

$$V_{\mathrm{m,i}} = \frac{5.25\ \mathrm{cm^3}}{70 \times 10^{-3}\ \mathrm{mol}} = 75.\bar{0}\ \mathrm{cm^3\ mol^{-1}}, \quad V_{\mathrm{m,f}} = \frac{6.29\ \mathrm{cm^3}}{70 \times 10^{-3}\ \mathrm{mol}} = 89.\bar{9}\ \mathrm{cm^3\ mol^{-1}}$$

and so $B\left(\dfrac{1}{V_{\mathrm{m,f}}} - \dfrac{1}{V_{\mathrm{m,i}}}\right) = (-28.7\ \mathrm{cm^3\ mol^{-1}}) \times \left(\dfrac{1}{89.9\ \mathrm{cm^3\ mol^{-1}}} - \dfrac{1}{75.0\ \mathrm{cm^3\ mol^{-1}}}\right)$

$$= 6.3\bar{4} \times 10^{-2}$$

Therefore, $w = (-21\bar{7}\text{ J}) \times \ln\left(\dfrac{6.29}{5.25}\right) + (21\bar{7}\text{ J}) \times (6.3\bar{4} \times 10^{-2}) = (-39.\bar{2}\text{ J}) + (13.8\text{ J}) = \boxed{-25\text{ J}}$

Since $\Delta U = q + w$ and $\Delta U = +83.5\text{ J}$, $q = \Delta U - w = (83.5\text{ J}) + (25\text{ J}) = \boxed{+109\text{ J}}$

$$\Delta H = \Delta U + \Delta(pV), \quad \text{with} \quad pV = nRT\left(1 + \frac{B}{V_\text{m}}\right)$$

$$\begin{aligned}\Delta(pV) &= nRTB\Delta\left(\frac{1}{V_\text{m}}\right) = nRTB\left(\frac{1}{V_\text{m,f}} - \frac{1}{V_\text{m,i}}\right), \quad \text{as } \Delta T = 0\\ &= (21\bar{7}\text{ J}) \times (6.3\bar{4} \times 10^{-2}) = 13.\bar{8}\text{ J}\end{aligned}$$

Therefore, $\Delta H = (83.5\text{ J}) + (13.\bar{8}\text{ J}) = \boxed{+97\text{ J}}$

P2.6 $$w = -\int_{V_1}^{V_2} p\,\mathrm{d}V \quad \text{with} \quad p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}\ [1.21\text{a}]$$

Therefore, $$w = -nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V - nb} + n^2a\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V^2} = \boxed{-nRT\ \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

This expression can be interpreted more readily if we assume $V \gg nb$, which is certainly valid at all but the highest pressures. Then, using the first term of the Taylor series expansion,

$$\ln(1 - x) = -x - \frac{x^2}{2}\cdots \quad \text{for } |x| \ll 1$$

$$\ln(V - nb) = \ln V + \ln\left(1 - \frac{nb}{V}\right) \approx \ln V - \frac{nb}{V}$$

and, after substitution

$$\begin{aligned}w &\approx -nRT\ln\left(\frac{V_2}{V_1}\right) + n^2bRT\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\\ &\approx -nRT\ln\left(\frac{V_2}{V_1}\right) - n^2(a - bRT)\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\\ &\approx +w_0 - n^2(a - bRT)\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = \text{perfect gas value } + \text{van der Waals correction.}\end{aligned}$$

w_0, the perfect gas value, is negative in expansion and positive in compression. Considering the correction term, in expansion $V_2 > V_1$, so $\left(\dfrac{1}{V_2} - \dfrac{1}{V_1}\right) < 0$. If attractive forces predominate, $a > bRT$ and the work done *by* the van der Waals gas is less in magnitude (less negative) than the perfect gas—the gas cannot easily expand. If repulsive forces predominate, $bRT > a$ and the work done *by* the van der Waals gas is greater in magnitude than the perfect gas—the gas easily expands. In the numerical calculations, consider a doubling of the initial volume.

(a) $$w_0 = -nRT\ln\left(\frac{V_f}{V_i}\right) = (-1.0\ \text{mol}^{-1})\times(8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})\times\ln\left(\frac{2.0\ \text{dm}^3}{1.0\ \text{dm}^3}\right)$$

$$w_0 = -1.7\overline{2}\times10^3\ \text{J} = \boxed{-1.7\ \text{kJ}}$$

(b) $$w = w_0 - (1.0\ \text{mol})^2\times[0-(5.11\times10^{-2}\ \text{dm}^3\text{mol}^{-1})\times(8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})]$$
$$\times\left(\frac{1}{2.0\ \text{dm}^3}-\frac{1}{1.0\ \text{dm}^3}\right) = (-1.7\overline{2}\times10^3\ \text{J})-(63\ \text{J}) = -1.7\overline{8}\times10^3\ \text{J} = \boxed{-1.8\ \text{kJ}}$$

(c) $$w = w_0 - (1.0\ \text{mol})^2\times(4.2\ \text{dm}^6\,\text{atm mol}^{-2})\times\left(\frac{1}{2.0\ \text{dm}^3}-\frac{1}{1.0\ \text{dm}^3}\right)$$

$$w = w_0 + 2.1\ \text{dm}^3\,\text{atm}$$
$$= (-1.7\overline{2}\times10^3\ \text{J}) + (2.1\ \text{dm}^3\,\text{atm})\times\left(\frac{1\ \text{m}}{10\ \text{dm}}\right)^3\times\left(\frac{1.01\times10^5\ \text{Pa}}{1\ \text{atm}}\right)$$
$$= (-1.7\overline{2}\times10^3\ \text{J}) + (0.21\times10^3\ \text{J}) = \boxed{-1.5\ \text{kJ}}$$

Schematically, the indicator diagrams for the cases (a), (b), and (c) would appear as in Figure 2.2. For case (b) the pressure is always greater than the perfect gas pressure and for case (c) always less. Therefore,

$$\int_{V_1}^{V_2} p\,\mathrm{d}V(\text{c}) < \int_{V_1}^{V_2} p\,\mathrm{d}V(\text{a}) < \int_{V_1}^{V_2} p\,\mathrm{d}V(\text{b})$$

and we see that $w(\text{b}) > w(\text{a}) > w(\text{c})$.

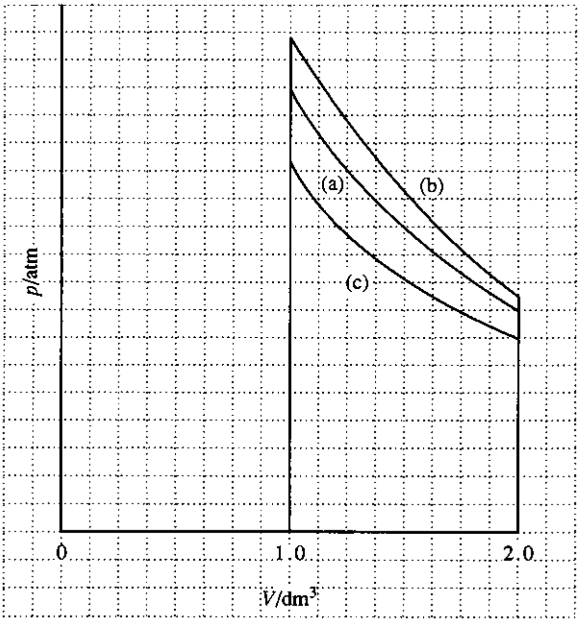


Figure 2.2

P2.8 The calorimeter is a constant-volume instrument as described in the text (Section 2.4), therefore

$$\Delta U = q_V$$

The calorimeter constant is determined from the data for the combustion of benzoic acid

$$\Delta U = \left(\frac{0.825\ \text{g}}{122.12\ \text{g mol}^{-1}}\right) \times (-3251\ \text{kJ mol}^{-1}) = -21.9\bar{6}\ \text{kJ}$$

Since $\Delta T = 1.940\ \text{K}$, $C = \dfrac{|q|}{\Delta T} = \dfrac{21.9\bar{6}\ \text{kJ}}{1.940\ \text{K}} = 11.3\bar{2}\ \text{kJ K}^{-1}$

For D-ribose, $\Delta U = -C\Delta T = -(11.3\bar{2}\ \text{kJ K}^{-1}) \times (0.910\ \text{K})$

Therefore, $\Delta_r U = \dfrac{\Delta U}{n} = -(11.3\bar{2}\ \text{kJ K}^{-1}) \times (0.910\ \text{K}) \times \left(\dfrac{150.13\ \text{g mol}^{-1}}{0.727\ \text{g}}\right) = -212\bar{7}\ \text{kJ mol}^{-1}$

The combustion reaction for D-ribose is

$$C_5H_{10}O_5(s) + 5\,O_2(g) \rightarrow 5\,CO_2(g) + 5\,H_2O(l)$$

Since there is no change in the number of moles of gas, $\Delta_r H = \Delta U$ [2.21]

The enthalpy of formation is obtained from the sum

	$\Delta H/(\text{kJ mol}^{-1})$
$5\,CO_2(g) + 5\,H_2O(l) \rightarrow C_5H_{10}O_5(s) + 5\,O_2(g)$	2127
$5\,C(s) + 5\,O_2(g) \rightarrow 5\,CO_2(g)$	$5 \times (-393.51)$
$5\,H_2(g) + \frac{2}{5}\,O_2(g) \rightarrow 5\,H_2O(l)$	$5 \times (-285.83)$
$5\,C(s) + 5\,H_2(g) + \frac{2}{5}\,O_2(g) \rightarrow C_5H_{10}O_5(s)$	-1270

Hence, $\Delta_f H = \boxed{-1270\ \text{kJ mol}^{-1}}$

P2.10 Data: methane–octane normal alkane combustion enthalpies

Species	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}
$\Delta_c H^\circ/(\text{kJ mol}^{-1})$	-890	-1560	-2220	-2878	-3537	-4163	-5471
$M/(\text{g mol}^{-1})$	16.04	30.07	44.10	58.13	72.15	86.18	114.23

Suppose that $\Delta_c H^\circ = kM^n$. There are two methods by which a regression analysis can be used to determine the values of k and n. If you have a software package that can perform a 'power fit' of the type $Y = aX^b$, the analysis is direct using $Y = \Delta_c H$ and $X = M$. Then, $k = a$ and $n = b$. Alternatively, taking the logarithm yields another equation—one of linear form

$$\ln|\Delta_c H^\circ| = \ln|k| + n \ln M, \quad \text{where } k < 0$$

This equation suggests a linear regression fit of $\ln(\Delta_c H^\circ)$ against $\ln M$ (Figure 2.3). The intercept is $\ln k$ and the slope is n. Linear regression fit

$\ln|k| = 4.2112$, standard deviation $= 0.0480$ $\quad k = -e^{4.2112} = \boxed{-67.44}$

$\boxed{n = 0.9253}$, standard deviation $= 0.0121$

$R = 1.000$

This is a good regression fit; essentially all of the variation is explained by the regression.

For decane the experimental value of $\Delta_c H^\circ$ equals −6772.5 kJ mol^{-1} (*CRC Handbook of Chemistry and Physics*). The predicted value is

$$\Delta_c H^\circ = kM^n = -67.44(142.28)^{(0.9253)}\ \text{kJ mol}^{-1} = \boxed{-6625.5\ \text{kJ mol}^{-1}}$$

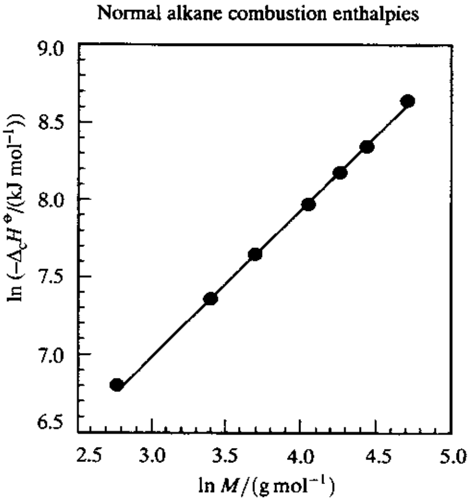


Figure 2.3

$$\text{Percentage error of prediction} = \left|\frac{-6772.5-(-6625.5)}{-6625.5}\right| \times 100$$

$$\text{Percentage error of prediction} = \boxed{2.17\%}$$

P2.12 (a) The magnitude of the energy released as heat is

$$q = -n\Delta_c H^\circ = -\frac{1.5\,\text{g}}{342.3\,\text{g mol}^{-1}} \times (-5645\ \text{kJ mol}^{-1}) = \boxed{+25\ \text{kJ}}$$

(b) Effective work available is ≈ 25 kJ × 0.25 = 6.2 kJ

Because $w = mgh$, and $m \approx 65$ kg

$$h \approx \frac{6.2 \times 10^3\ \text{J}}{65\ \text{kg} \times 9.81\ \text{m s}^{-2}} = \boxed{9.7\ \text{m}}$$

(c) The energy released as heat is

$$q = -\Delta_r H = -n\Delta_c H^\circ = -\left(\frac{2.5\ \text{g}}{180\ \text{g mol}^{-1}}\right) \times (-2808\ \text{kJ mol}^{-1}) = \boxed{39\ \text{kJ}}$$

(d) If one-quarter of this energy were available as work a 65 kg person could climb to a height h given by

$$\tfrac{1}{4}q = w = mgh \quad \text{so} \quad h = \frac{q}{4mg} = \frac{39 \times 10^3\ \text{J}}{4(65\ \text{kJ}) \times (9.8\ \text{m s}^{-2})} = \boxed{15\ \text{m}}$$

P2.14 $H_3O^+(aq) + NaCH_3COO \cdot 3\,H_2O(s) \rightarrow Na^+(aq) + CH_3COOH(aq) + 4\,H_2O(l)$

$n_{salt} = m_{salt}/M_{salt} = 1.3584\ \text{g}/(136.08\ \text{g mol}^{-1}) = 0.0099824\ \text{mol}$

Application of eqns 2.13 and 2.19b gives:

$$\begin{aligned}\Delta_r H_m &= -\Delta_{calorimeter} H/n_{salt} = -C_{calorimeter+contents}\Delta T/n_{salt}\\ &= -(C_{calorimeter} + C_{solution})\Delta T/n_{salt}\\ &= -(91.0\ \text{J K}^{-1} + 4.144\ \text{J K}^{-1}\text{cm}^{-3} \times 100\ \text{cm}^3) \times (-0.397\ \text{K})/0.0099824\ \text{mol}\\ &= 20.1\ \text{kJ mol}^{-1}\end{aligned}$$

Application of eqn 2.32 gives:

$$\begin{aligned}\Delta_r H^{\ominus} = {} & \Delta_f H^{\ominus}(Na^+,aq) + \Delta_f H^{\ominus}(CH_3COOH,aq) + 3\Delta_f H^{\ominus}(H_2O,l)\\ & -\Delta_f H^{\ominus}(H^+,aq) - \Delta_f H^{\ominus}(NaCH_3COO \cdot 3H_2O,s)\end{aligned}$$

(where the water coefficient is 3 not 4 because one water in the chemical equation is part of the hydrated hydrogen ion). Solving for $\Delta_f H^{\ominus}(Na^+,aq)$ and substituting $\Delta_f H^{\ominus}$ values found in Tables 2.6 and 2.8 gives

$$\begin{aligned}\Delta_f H^{\ominus}(Na^+,aq) = {} & \Delta_r H^{\ominus} - \Delta_f H^{\ominus}(CH_3COOH,aq) - 3\Delta_f H^{\ominus}(H_2O,l)\\ & + \Delta_f H^{\ominus}(H^+,aq) + \Delta_f H^{\ominus}(NaCH_3COO \cdot 3H_2O,s)\end{aligned}$$

$$\begin{aligned}\Delta_f H^{\ominus}(Na^+,aq) &= \{20.1 - (-485.76) - 3(-285.83) + (0) + (-1604)\}\ \text{kJ mol}^{-1}\\ &= \boxed{-241\ \text{kJ mol}^{-1}}\end{aligned}$$

P2.16 We must relate the formation of $DyCl_3$

$Dy(s) + 1.5\,Cl_2(g) \rightarrow DyCl_3(s)$

to the three reactions for which we have information. This reaction can be seen as a sequence of reaction(2), three times reaction(3), and the reverse of reaction(1), so

$$\Delta_f H^{\ominus}(DyCl_3,s) = \Delta_r H^{\ominus}(2) + 3\Delta_r H^{\ominus}(3) - \Delta_r H^{\ominus}(1),$$

$$\begin{aligned}\Delta_f H^{\ominus}(DyCl_3,s) &= [-699.43 + 3(-158.31) - (-180.06)]\ \text{kJ mol}^{-1}\\ &= \boxed{-994.30\ \text{kJ mol}^{-1}}\end{aligned}$$

P2.18 (a)
$$\begin{aligned}\Delta_r H^{\ominus} &= \Delta_f H^{\ominus}(SiH_3OH) - \Delta_f H^{\ominus}(SiH_4) - \tfrac{1}{2}\Delta_f H^{\ominus}(O_2)\\ &= [-282 - 34.3 - \tfrac{1}{2}(0)]\ \text{kJ mol}^{-1}\\ &= \boxed{-316.3\ \text{kJ mol}^{-1}}\end{aligned}$$

(b)
$$\begin{aligned}\Delta_r H^{\ominus} &= \Delta_f H^{\ominus}(SiH_2O) - \Delta_f H^{\ominus}(H_2O) - \Delta_f H^{\ominus}(SiH_4) - \Delta_f H^{\ominus}(O_2)\\ &= [-98.3 + (-285.83) - 34.3 - 0]\ \text{kJ mol}^{-1}\\ &= \boxed{-418.43\ \text{kJ mol}^{-1}}\end{aligned}$$

(c)
$$\begin{aligned}\Delta_r H^{\ominus} &= \Delta_f H^{\ominus}(SiH_2O) - \Delta_f H^{\ominus}(SiH_3OH) - \Delta_f H^{\ominus}(H_2)\\ &= [-98.3 - (-282) - 0]\ \text{kJ mol}^{-1}\\ &= \boxed{183.7\ \text{kJ mol}^{-1}}\end{aligned}$$

P2.20

$$\mathrm{d}H=\left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T+\left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p, \quad \text{or} \quad \mathrm{d}H=\left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \quad \text{[constant temperature]}$$

$$\left(\frac{\partial H_\mathrm{m}}{\partial p}\right)_T=-\mu C_{p,\mathrm{m}} \;[\textit{Justification } 2.2]=-\left(\frac{2a}{RT}-b\right)$$

$$=-\left(\frac{(2)\times(3.60\ \mathrm{dm^6\,atm\,mol^{-2}})}{(0.0821\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})\times(300\ \mathrm{K})}-0.044\ \mathrm{dm^3\,mol^{-1}}\right)=-0.248\overline{3}\ \mathrm{dm^3\,mol^{-1}}$$

$$\Delta H=\int_{p_\mathrm{i}}^{p_\mathrm{f}}\mathrm{d}H=\int_{p_\mathrm{i}}^{p_\mathrm{f}}(-0.248\overline{3}\ \mathrm{dm^3\,mol^{-1}})\,\mathrm{d}p=-0.248\overline{3}(p_\mathrm{f}-p_\mathrm{i})\ \mathrm{dm^3\,mol^{-1}}$$

$$p=\frac{RT}{V_\mathrm{m}-b}-\frac{a}{V_\mathrm{m}^2}\ [1.21\mathrm{b}]$$

$$p_\mathrm{i}=\left(\frac{(0.0821\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})\times(300\ \mathrm{K})}{(20.0\ \mathrm{dm^3\,mol^{-1}})-(0.044\ \mathrm{dm^3\,mol^{-1}})}\right)-\left(\frac{3.60\ \mathrm{dm^6\,atm\,mol^{-2}}}{(20.0\ \mathrm{dm^3\,mol^{-1}})^2}\right)=1.22\overline{5}\ \mathrm{atm}$$

$$p_\mathrm{f}=\left(\frac{(0.0821\ \mathrm{dm^3\,atm}\,K^{-1}\,\mathrm{mol^{-1}})\times(300\ \mathrm{K})}{(10.0\ \mathrm{dm^3\,mol^{-1}})-(0.044\ \mathrm{dm^3\,mol^{-1}})}\right)-\left(\frac{3.60\ \mathrm{dm^6\,atm\,mol^{-2}}}{(10.0\ \mathrm{dm^3\,mol^{-1}})^2}\right)=2.43\overline{8}\ \mathrm{atm}$$

$$\Delta H=(-0.248\overline{3}\ \mathrm{dm^3\,mol^{-1}})\times(2.43\overline{8}\ \mathrm{atm}-1.225\ \mathrm{atm})$$

$$=(-0.301\ \mathrm{dm^3\,atm\,mol^{-1}})\times\left(\frac{1\ \mathrm{m}}{10\ \mathrm{dm}}\right)^3\times\left(\frac{1.013\times10^5\ \mathrm{Pa}}{\mathrm{atm}}\right)=\boxed{-30.5\ \mathrm{J\,mol^{-1}}}$$

Solutions to theoretical problems

P2.22 A function has an exact differential if its mixed partial derivatives are equal. That is, $f(x,y)$ has an exact differential if

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)=\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

(a) $$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)=\frac{\partial}{\partial y}(2xy)=2x \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)=\frac{\partial}{\partial x}(x^2+6y)=2x$$

(b) $$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)=\frac{\partial}{\partial y}(\cos xy-xy\sin xy)$$

$$=-x\sin xy-x\sin xy-x^2y\cos xy=-2x\sin xy-x^2y\cos xy$$

and $$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)=\frac{\partial}{\partial x}(-x^2\sin xy)=-2x\sin xy-x^2y\cos xy$$

(c) $$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)=\frac{\partial}{\partial y}(3x^2y^2)=6x^2y \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)=\frac{\partial}{\partial x}(2x^3y)=6x^2y$$

(d) $$\frac{\partial}{\partial t}\left(\frac{\partial f}{\partial s}\right)=\frac{\partial}{\partial t}(te^s+1)=e^s \quad \text{and} \quad \frac{\partial}{\partial s}\left(\frac{\partial f}{\partial t}\right)=\frac{\partial}{\partial s}(2t+e^s)=e^s$$

P2.24 $$C_V=\left(\frac{\partial U}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T=\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T=\left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V}$$ (derivatives may be taken in any order)

$\left(\frac{\partial U}{\partial V}\right)_T=0$ for a perfect gas [Section 2.11(b)]

Hence, $\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T=0}$

Likewise $C_p=\left(\frac{\partial H}{\partial T}\right)_p$, so $\boxed{\left(\frac{\partial C_p}{\partial p}\right)_T=\left(\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial T}\right)_p\right)_T=\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial p}\right)_T\right)_p}$

$\left(\frac{\partial H}{\partial p}\right)_T=0$ for a perfect gas.

Hence, $\left(\frac{\partial C_p}{\partial p}\right)_T=0.$

P2.26 Using Euler's chain relationship and the reciprocal identity [MB2.3c]

$$\left(\frac{\partial p}{\partial T}\right)_V=-\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

Substituting into the given expression for C_p-C_V

$$C_p-C_V=-T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p^2$$

Using the reciprocal identity again

$$C_p-C_V=-\frac{T\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T}$$

For a perfect gas, $pV=nRT$, so

$$\left(\frac{\partial V}{\partial T}\right)_p^2=\left(\frac{nR}{p}\right)^2 \quad \text{and} \quad \left(\frac{\partial V}{\partial p}\right)_T=-\frac{nRT}{p^2}$$

so $$C_p-C_V=\frac{-T\left(\frac{nR}{p}\right)^2}{-\frac{nRT}{p^2}}=\boxed{nR}$$

P2.28 This problem is the same as Problem 2.25(b). The solution is the same as presented for that problem.

P2.30 (a) $V = V(p,T)$, hence, $\mathrm{d}V = \boxed{\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T}$

Likewise $p = p(V,T)$, so $\mathrm{d}p = \boxed{\left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T}$

(b) We use $\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p$ [2.42] and $\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T$ [2.43] and obtain

$$\mathrm{d}\ln V = \frac{1}{V}\mathrm{d}V = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T = \boxed{-\kappa_T\,\mathrm{d}p + \alpha\,\mathrm{d}T}.$$

Likewise $\mathrm{d}\ln p = \frac{\mathrm{d}p}{p} = \frac{1}{p}\left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V + \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T$

We express $\left(\frac{\partial p}{\partial V}\right)_T$ in terms of κ_T:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\left[V\left(\frac{\partial p}{\partial V}\right)_T\right]^{-1} \quad \text{so} \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{\kappa_T V}$$

We express $\left(\frac{\partial p}{\partial T}\right)_V$ in terms of κ_T and α

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1 \quad \text{so} \quad \left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

$$\text{so} \quad \mathrm{d}\ln p = -\frac{\mathrm{d}V}{p\kappa_T V} + \frac{\alpha\,\mathrm{d}T}{p\kappa_T} = \boxed{\frac{1}{p\kappa_T}\left(\alpha\,\mathrm{d}T - \frac{\mathrm{d}V}{V}\right)}$$

P2.32

$$\begin{aligned} w &= -\int_{V_1}^{V_2} p\,\mathrm{d}V = -nRT\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V-nb} + n^2a\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V^2} \\ &= -nRT\ln\left(\frac{V_2-nb}{V_1-nb}\right) - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right) \end{aligned}$$

By multiplying and dividing the value of each variable by its critical value we obtain

$$w = -nR\times\left(\frac{T}{T_c}\right)T_c\times\ln\left(\frac{\frac{V_2}{V_c}-\frac{nb}{V_c}}{\frac{V_1}{V_c}-\frac{nb}{V_c}}\right) - \left(\frac{n^2a}{V_c}\right)\times\left(\frac{V_c}{V_2}-\frac{V_c}{V_1}\right)$$

$$T_r = \frac{T}{T_c},\quad V_r = \frac{V}{V_c},\quad T_c = \frac{8a}{27Rb},\quad V_c = 3nb \quad \text{[Table 1.7]}$$

$$w = -\left(\frac{8na}{27b}\right)\times(T_r)\times\ln\left(\frac{V_{r,2}-\frac{1}{3}}{V_{r,1}-\frac{1}{3}}\right)-\left(\frac{na}{3b}\right)\times\left(\frac{1}{V_{r,2}}-\frac{1}{V_{r,1}}\right)$$

The van der Waals constants can be eliminated by defining $w_r = \frac{3bw}{a}$, then $w = \frac{aw_r}{3b}$ and

$$w_r = \boxed{-\frac{8}{9}nT_r\ln\left(\frac{V_{r,2}-1/3}{V_{r,1}-1/3}\right)-n\left(\frac{1}{V_{r,2}}-\frac{1}{V_{r,1}}\right)}$$

Along the critical isotherm, $T_r = 1$, $V_{r,1} = 1$, and $V_{r,2} = x$. Hence,

$$\frac{w_r}{n} = \boxed{-\frac{8}{9}\ln\left(\frac{3x-1}{2}\right)-\frac{1}{x}+1}$$

P2.34 $$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H \quad [2.50]$$

Use of Euler's chain relationship [MB2.4] yields

$$\mu = -\frac{\left(\frac{\partial H_m}{\partial p}\right)_T}{C_{p,m}} \quad [\textit{Justification 2.2}]$$

$$\left(\frac{\partial H_m}{\partial p}\right)_T = \left(\frac{\partial U_m}{\partial p}\right)_T + \left[\frac{\partial(pV_m)}{\partial p}\right]_T = \left(\frac{\partial U_m}{\partial V_m}\right)_T\left(\frac{\partial V_m}{\partial p}\right)_T + \left[\frac{\partial(pV_m)}{\partial p}\right]_T$$

Use the virial expansion of the van der Waals equation in terms of p. (See the solution to Problem 1.9.) Now let us evaluate some of these derivatives.

$$\left(\frac{\partial U_m}{\partial V_m}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T = \pi_T = \frac{a}{V_m^2} \quad \text{[Exercise 2.31a]}$$

$$pV_m = RT\left[1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)p+\cdots\right]$$

$$\left[\frac{\partial(pV_m)}{\partial p}\right]_T \approx b-\frac{a}{RT},\quad \left(\frac{\partial V_m}{\partial p}\right)_T \approx -\frac{RT}{p^2}$$

Substituting $\left(\frac{\partial H_m}{\partial p}\right)_T \approx \left(\frac{a}{V_m^2}\right)\times\left(-\frac{RT}{p^2}\right)+\left(b-\frac{a}{RT}\right) \approx \frac{-aRT}{(pV_m)^2}+\left(b-\frac{a}{RT}\right)$

Since $\left(\frac{\partial H_{\mathrm{m}}}{\partial p}\right)_T$ is in a sense a correction term, that is, it approaches zero for a perfect gas, little error will be introduced by the approximation, $(pV_{\mathrm{m}})^2 = (RT)^2$.

Thus, $\left(\frac{\partial H_{\mathrm{m}}}{\partial p}\right)_T \approx \left(-\frac{a}{RT}\right) + \left(b - \frac{a}{RT}\right) = \left(b - \frac{2a}{RT}\right)$ and $\mu = \frac{\left(\frac{2a}{RT} - b\right)}{C_{p,\mathrm{m}}}$

P2.36

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V\left(\frac{\partial T}{\partial V}\right)_p} \text{ [reciprocal identity, MB2.3b]}$$

$$\alpha = \frac{1}{V} \times \frac{1}{\left(\frac{T}{V - nb}\right) - \left(\frac{2na}{RV^3}\right) \times (V - nb)} \text{ [Problem 2.35]}$$

$$= \boxed{\frac{(RV^2) \times (V - nb)}{(RTV^3) - (2na) \times (V - nb)^2}}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{-1}{V\left(\frac{\partial p}{\partial V}\right)_T} \text{ [reciprocal identity]}$$

$$\kappa_T = -\frac{1}{V} \times \frac{1}{\left(\frac{-nRT}{(V - nb)^2}\right) + \left(\frac{2n^2 a}{V^3}\right)} \text{ [Problem 2.35]}$$

$$= \boxed{\frac{V^2(V - nb)^2}{nRTV^3 - 2n^2 a(V - nb)^2}}$$

Then, $\frac{\kappa_T}{\alpha} = \frac{V - nb}{nR}$, implying that $\kappa_T R = \alpha(V_{\mathrm{m}} - b)$

Alternatively, from the definitions of α and κ_T above

$$\frac{\kappa_T}{\alpha} = \frac{-\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_p} = \frac{-1}{\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p} \text{ [reciprocal identity]}$$

$$= \left(\frac{\partial T}{\partial p}\right)_V \text{ [Euler chain relation]} = \frac{V - nb}{nR} \text{ [Problem 2.35]},$$

$$\kappa_T R = \frac{\alpha(V - nb)}{n}$$

Hence, $\kappa_T R = \alpha(V_{\mathrm{m}} - b)$.

P2.38 Work with the left-hand side of the relationship to be proved and show that after manipulation using the general relationships between partial derivatives and the given equation for $\left(\dfrac{\partial U}{\partial V}\right)_T$, the right-hand side is produced.

$$\left(\frac{\partial H}{\partial p}\right)_T=\left(\frac{\partial H}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \text{ [change of variable]}$$

$$=\left(\frac{\partial(U+pV)}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \text{ [definition of } H\text{]}$$

$$=\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T+\left(\frac{\partial(pV)}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T$$

$$=\left\{T\left(\frac{\partial p}{\partial T}\right)_V-p\right\}\left(\frac{\partial V}{\partial p}\right)_T+\left(\frac{\partial(pV)}{\partial p}\right)_T\left[\text{equation for }\left(\frac{\partial U}{\partial V}\right)_T\right]$$

$$=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T-p\left(\frac{\partial V}{\partial p}\right)_T+V+p\left(\frac{\partial V}{\partial p}\right)_T$$

$$=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T+V=\frac{-T}{\left(\dfrac{\partial T}{\partial V}\right)_p}+V \text{ [chain relation]}$$

$$=\boxed{-T\left(\frac{\partial V}{\partial T}\right)_p+V} \text{ [reciprocal identity]}$$

P2.40 $c_s=\left(\dfrac{RT\gamma}{M}\right)^{1/2}$, $p=\rho\dfrac{RT}{M}$, so $\dfrac{RT}{M}=\dfrac{p}{\rho}$; hence $\boxed{c_s=\left(\dfrac{\gamma p}{\rho}\right)^{1/2}}$

For argon, $\gamma=\frac{5}{3}$, so $c=\left(\dfrac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})\times(298\text{ K})\times\frac{5}{3}}{39.95\times10^{-3}\text{ kg mol}^{-1}}\right)^{1/2}=\boxed{322\text{ m s}^{-1}}$

Solutions to applications

P2.42 (a) $q_V=-n\Delta_c U^{\ominus}$, hence

(ii) $\Delta_c U^{\ominus}=\dfrac{-q_V}{n}=\dfrac{-C\Delta T}{n}=\dfrac{-MC\Delta T}{m}$, where m is sample mass and M molar mass

so $\Delta_c U^{\ominus}=-\dfrac{(180.16\text{ g mol}^{-1})\times(641\text{ J K}^{-1})\times(7.793\text{ K})}{0.3212\text{ g}}=\boxed{-280\bar{2}\text{ kJ mol}^{-1}}$

(i) The complete aerobic oxidation is

$C_6H_{12}O_6(s)+6\,O_2(g)\rightarrow 6\,CO_2(g)+6\,H_2O(l)$

Since there is no change in the number of moles of gas, $\Delta_r H^\ominus = \Delta_r U^\ominus$ [2.21] and

$$\Delta_c H^\ominus = \Delta_c U^\ominus = \boxed{-280\bar{2}\text{ kJ mol}^{-1}}$$

(iii) $\Delta_c H^\ominus = 6\Delta_f H^\ominus(\text{CO}_2,\text{g}) + 6\Delta_f H^\ominus(\text{H}_2\text{O},\text{l}) - \Delta_f H^\ominus(\text{C}_6\text{H}_{12}\text{O}_6,\text{s}) - 6\Delta_f H^\ominus(\text{O}_2,\text{g})$

so $\Delta_f H^\ominus(\text{C}_6\text{H}_{12}\text{O}_6,\text{s}) = 6\Delta_f H^\ominus(\text{CO}_2,\text{g}) + 6\Delta_f H^\ominus(\text{H}_2\text{O},\text{l}) - 6\Delta_f H^\ominus(\text{O}_2,\text{g}) - \Delta_c H^\ominus$

$$\begin{aligned}\Delta_f H^\ominus(\text{C}_6\text{H}_{12}\text{O}_6,\text{s}) &= [6(-393.51) + 6(-285.83) - 6(0) - (-280\bar{2})]\text{ kJ mol}^{-1}\\ &= \boxed{-127\bar{4}\text{ kJ mol}^{-1}}\end{aligned}$$

(b) The anaerobic glycolysis to lactic acid is

$$\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\ \text{CH}_3\text{CH(OH)COOH}$$

$$\begin{aligned}\Delta_r H^\ominus &= 2\Delta_f H^\ominus(\text{lactic acid}) - \Delta_f H^\ominus(\text{glucose})\\ &= \{(2)\times(-694.0) - (-127\bar{4})\}\text{ kJ mol}^{-1} = -11\bar{4}\text{ kJ mol}^{-1}\end{aligned}$$

Therefore, aerobic oxidation $\boxed{\text{is more exothermic by } 268\bar{8}\text{ kJ mol}^{-1}}$ than glycolysis.

P2.44 The coefficient of thermal expansion is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \approx \frac{\Delta V}{V\Delta T} \quad \text{so} \quad \Delta V \approx \alpha V \Delta T$$

This change in volume is equal to the change in height (sea level rise, Δh) times the area of the ocean (assuming that area remains constant). We will use α of pure water, although the oceans are complex solutions. For a 2°C rise in temperature

$$\Delta V = (2.1\times10^{-4}\text{ K}^{-1})\times(1.37\times10^{9}\text{ km}^3)\times(2.0\text{ K}) = 5.8\times10^{5}\text{ km}^3$$

$$\text{so}\quad \Delta h = \frac{\Delta V}{A} = 1.6\times10^{-3}\text{ km} = \boxed{1.6\text{ m}}$$

Since the rise in sea level is directly proportional to the rise in temperature, $\Delta T = 1$°C would lead to $\Delta h = \boxed{0.80\text{ m}}$ and $\Delta T = 3.5$°C would lead to $\Delta h = \boxed{2.8\text{ m}}$.

COMMENT. More detailed models of climate change predict somewhat smaller rises, but the same order of magnitude.

P2.46 We compute μ from

$$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

and we estimate $\left(\frac{\partial H}{\partial p}\right)_T$ from the enthalpy and pressure data. We are given both enthalpy and heat capacity data on a mass basis rather than a molar basis; however, the masses will cancel, so we need not convert to a molar basis.

(a) At 300 K

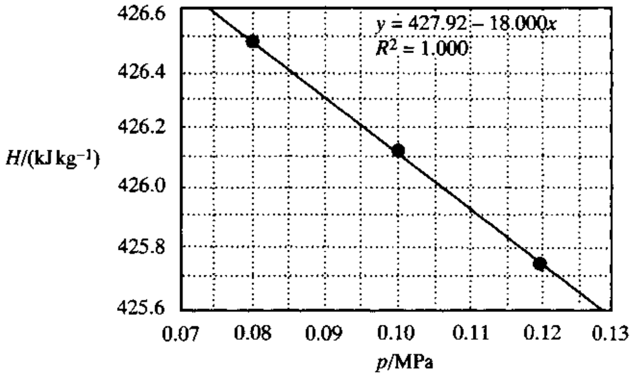


Figure 2.4(a)

The regression analysis gives the slope as $-18.0\ \mathrm{J\ g^{-1}\ MPa^{-1}} \approx \left(\dfrac{\partial H}{\partial p}\right)_T$ (see Figure 2.4(a))

$$\text{so}\quad \mu = -\frac{-18.0\ \mathrm{kJ\ kg^{-1}\ MPa^{-1}}}{0.7649\ \mathrm{kJ\ kg^{-1}\ K^{-1}}} = \boxed{23.5\ \mathrm{K\ MPa^{-1}}}$$

(b) At 350 K

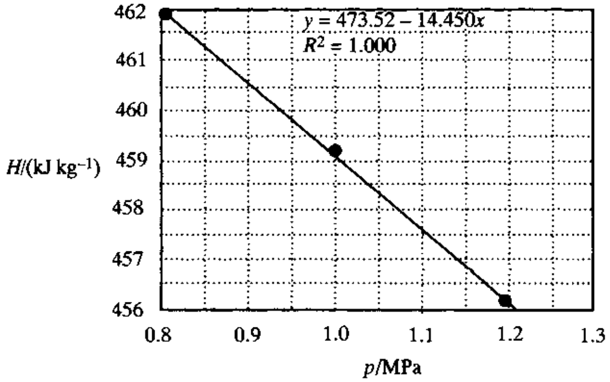


Figure 2.4(b)

The regression analysis gives the slope as $-14.5\ \mathrm{J\ g^{-1}\ MPa^{-1}} \approx \left(\dfrac{\partial H}{\partial p}\right)_T$ (see Figure 2.4(b))

$$\text{so}\quad \mu = -\frac{-14.5\ \mathrm{kJ\ kg^{-1}\ MPa^{-1}}}{1.0392\ \mathrm{kJ\ kg^{-1}\ K^{-1}}} = \boxed{14.0\ \mathrm{K\ MPa^{-1}}}$$

3 The second law

Answers to discussion questions

D3.2 The device proposed uses geothermal heat (energy) and appears to be similar to devices currently in existence for heating and lighting homes. As long as the amount of heat extracted from the hot source (the ground) is not less than the sum of the amount of heat discarded to the surroundings (by heating the home and operating the steam engine) and of the amount of work done by the engine to operate the heat pump, this device is possible; at least, it does not violate the first law of thermodynamics. However, the feasibility of the device needs to be tested from the point of view of the second law as well. There are various equivalent versions of the second law, and some are more directly useful in this case than others. On first analysis, it might seem that the net result of the operation of this device is the complete conversion of heat into the work done by the heat pump. This work is the difference between the heat absorbed from the surroundings and the heat discharged to the surroundings, and all of that difference has been converted to work. We might, then, conclude that this device violates the second law in the form stated in the introduction to Chapter 3 and therefore that it cannot operate as described. However, we must carefully examine the exact wording of the second law. The key words are 'sole result'. Another slightly different, although equivalent, wording of Kelvin's statement is the following: 'It is impossible by a cyclic process to take heat from a reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir.' So as long as some heat is discharged to surroundings colder than the geothermal source during its operation, there is no reason why this device should not work. A detailed analysis of the entropy changes associated with this device follows (see Figure 3.1).

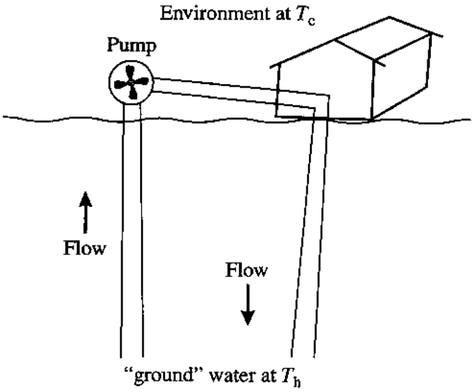


Figure 3.1 C_V and C_p are the temperature-dependent heat capacities of water

Three things must be considered in an analysis of the geothermal heat pump: Is it forbidden by the first law? Is it forbidden by the second law? Is it efficient?

$$\Delta E_{\text{tot}} = \Delta E_{\text{water}} + \Delta E_{\text{ground}} + \Delta E_{\text{environment}}$$

$$\Delta E_{\text{water}} = 0$$

$$\Delta E_{\text{ground}} = -C_V(T_{\text{h}})\{T_{\text{h}} - T_{\text{c}}\}$$

$$\Delta E_{\text{environment}} = -C_V(T_{\text{h}})\{T_{\text{h}} - T_{\text{c}}\}$$

adding terms, we find that $\Delta E_{\text{tot}} = 0$, which means that the first law is satisfied for any value of T_{h} and T_{c}:

$$\Delta S_{\text{tot}} = \Delta S_{\text{water}} + \Delta S_{\text{ground}} + \Delta S_{\text{environment}}$$

$$\Delta S_{\text{water}} = 0$$

$$\Delta S_{\text{ground}} = \frac{q_{\text{ground}}}{T_{\text{h}}} = \frac{-C_p(T_{\text{h}})\{T_{\text{h}} - T_{\text{c}}\}}{T_{\text{h}}}$$

$$\Delta S_{\text{environment}} = \frac{q_{\text{environment}}}{T_{\text{c}}} = \frac{C_p(T_{\text{c}})\{T_{\text{h}} - T_{\text{c}}\}}{T_{\text{c}}}$$

Adding terms and estimating that $C_p(T_{\text{h}}) \approx C_p(T_{\text{c}}) = C_p$, we find that

$$\Delta S_{\text{tot}} = C_p\{T_{\text{h}} - T_{\text{c}}\}\left\{\frac{1}{T_{\text{c}}} - \frac{1}{T_{\text{h}}}\right\}$$

This expression satisfies the second law ($\Delta S_{\text{tot}} > 0$) only when $T_{\text{h}} > T_{\text{c}}$. We can conclude that, if the proposal involves collecting heat from environmentally cool ground water and using the energy to heat a home or to perform work, the proposal cannot succeed no matter what level of sophisticated technology is applied. Should the 'ground' water be collected from deep within the Earth so that $T_{\text{h}} > T_{\text{c}}$, the resultant geothermal pump is feasible. However, the efficiency, given by eqn 3.10, must be high to compete with fossil fuels because high installation costs must be recovered during the lifetime of the apparatus.

$$\eta_{\text{rev}} = 1 - \frac{T_{\text{c}}}{T_{\text{h}}}$$

With $T_{\text{c}} \approx 273$ K and $T_{\text{h}} = 373$ K (the highest value possible at 1 bar), $\eta_{\text{rev}} = 0.268$. At most, about 27% of the extracted heat is available to do work, including driving the heat pump. The concept works especially well in Iceland, where geothermal springs bring boiling water to the surface.

D3.4 All of these expressions are obtained from a combination of the first law of thermodynamics with the Clausius inequality in the form $T\mathrm{d}S \geq \mathrm{d}q$ (as was done at the start of *Justification 3.2*.) It may be written as

$$-\mathrm{d}U - p_{\text{ex}}\mathrm{d}V + \mathrm{d}w_{\text{add}} + T\mathrm{d}S \geq 0$$

where we have divided the work into pressure–volume work and additional work. Under conditions of constant energy and volume and no additional work, that is, an isolated system, this relationship reduces to

$$\mathrm{d}S \geq 0$$

which is equivalent to $\Delta S_{\text{tot}} = \Delta S_{\text{universe}} \geq 0$. (The universe is an isolated system.)

Under conditions of constant temperature and volume, with no additional work, the relationship reduces to

$$\mathrm{d}A \leq 0,$$

where A is defined as $U - TS$.

Under conditions of constant temperature and pressure, with no additional work, the relationship reduces to

$$\mathrm{d}G \leq 0,$$

where G is defined as $U + pV - TS = H - TS$.

In all of these relationships, choosing the inequality provides the criteria for *spontaneous change*. Choosing the equal sign gives us the criteria for *equilibrium* under the conditions specified.

D3.6 See the solution to Exercise 2.31(a) and Example 3.6, where it is demonstrated that $\pi_T = a/V_{\mathrm{m}}^2$ for a van der Waals gas. Therefore, there is no dependence on b for a van der Waals gas. The internal pressure results from attractive interactions alone. For van der Waals gases and liquids with strong attractive forces (large a) at small volumes, the internal pressure can be very large.

D3.8 The relationship $(\partial G/\partial T)_p = -S$ shows that the Gibbs function of a system decreases with T at constant P in proportion to the magnitude of its entropy. This makes good sense when one considers the definition of G, which is $G = U + pV - TS$. Hence, G is expected to decrease with T in proportion to S when p is constant. Furthermore, an increase in temperature causes entropy to increase according to

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \mathrm{d}q_{\text{rev}}/T$$

The corresponding increase in molecular disorder causes a decline in the Gibbs energy. (Entropy is always positive.)

Solutions to exercises

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

E3.1(b)

$$\Delta S = \int \frac{\mathrm{d}q_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

(a) $$\Delta S = \frac{50 \times 10^3\ \mathrm{J}}{273\ \mathrm{K}} = \boxed{1.8 \times 10^2\ \mathrm{J\ K^{-1}}}$$

(b) $$\Delta S = \frac{50 \times 10^3\ \mathrm{J}}{(70 + 273)\ \mathrm{K}} = \boxed{1.5 \times 10^2\ \mathrm{J\ K^{-1}}}$$

E3.2(b) At 250 K, the entropy is equal to its entropy at 298 K plus ΔS, where

$$\Delta S = \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int \frac{C_{V,\mathrm{m}}\,\mathrm{d}T}{T} = C_{V,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_\mathrm{i}}$$

so $S = 154.84\ \mathrm{J\ K^{-1}\ mol^{-1}} + [(20.786 - 8.3145)\ \mathrm{J\ K^{-1}\ mol^{-1}}] \times \ln \dfrac{250\ \mathrm{K}}{298\ \mathrm{K}}$

$$S = \boxed{152.65\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

E3.3(b) However, the change occurred ΔS has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2):

$$\Delta S = \Delta S_1 + \Delta S_2$$

For the first step

$$\Delta S_1 = \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int \frac{C_{p,\mathrm{m}}\,\mathrm{d}T}{T} = C_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_\mathrm{i}}$$

$$\Delta S_1 = (2.00\ \mathrm{mol}) \times \left(\frac{7}{2}\right) \times (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln \frac{(135 + 273)\ \mathrm{K}}{(25 + 273)\ \mathrm{K}} = 18.3\ \mathrm{J\ K^{-1}}$$

and for the second

$$\Delta S_2 = \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \frac{q_{\mathrm{rev}}}{T}$$

where $q_{\mathrm{rev}} = -w = \displaystyle\int p\,\mathrm{d}V = nRT \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} = nRT \ln \frac{p_\mathrm{i}}{p_\mathrm{f}}$

so $\Delta S_2 = nR \ln \dfrac{p_\mathrm{i}}{p_\mathrm{f}} = (2.00\ \mathrm{mol}) \times (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln \dfrac{1.50\ \mathrm{atm}}{7.00\ \mathrm{atm}} = -25.6\ \mathrm{J\ K^{-1}}$

$$\Delta S = (18.3 - 25.6)\ \mathrm{J\ K^{-1}} = \boxed{-7.3\ \mathrm{J\ K^{-1}}}$$

The heat lost in step 2 was more than the heat gained in step 1, resulting in a net loss of entropy. Alternatively, the ordering represented by confining the sample to a smaller volume in step 2 overcame the disordering represented by the temperature rise in step 1. A negative entropy change is allowed for a system as long as an increase in entropy elsewhere results in $\Delta S_{\mathrm{total}} > 0$.

E3.4(b) $q = q_{\mathrm{rev}} = 0$ [adiabatic reversible process]

$$\Delta S = \int_\mathrm{i}^\mathrm{f} \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \boxed{0}$$

$$\Delta U = nC_{V,\mathrm{m}}\Delta T = (2.00\ \mathrm{mol}) \times (27.5\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (300 - 250)\ \mathrm{K}$$

$$= 2750\ \mathrm{J} = \boxed{+2.75\ \mathrm{kJ}}$$

$$w = \Delta U - q = 2.75\ \mathrm{kJ} - 0 = \boxed{2.75\ \mathrm{kJ}}$$

$$\Delta H = nC_{p,\mathrm{m}}\Delta T$$

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R = (27.5\ \mathrm{J\ K^{-1}\,mol^{-1}} + 8.314\ \mathrm{J\ K^{-1}\,mol^{-1}}) = 35.81\overline{4}\ \mathrm{J\ K^{-1}\,mol^{-1}}$$

So, $\Delta H = (2.00\ \mathrm{mol}) \times (35.81\overline{4}\ \mathrm{J\ K^{-1}\,mol^{-1}}) \times (+50\ \mathrm{K}) = 358\overline{1.4}\ \mathrm{J} = \boxed{3.58\ \mathrm{kJ}}$

E3.5(b) Since the masses are equal and the heat capacity is assumed constant, the final temperature will be the average of the two initial temperatures,

$$T_\mathrm{f} = \tfrac{1}{2}(200°\mathrm{C} + 25°\mathrm{C}) = 112.\overline{5}°\mathrm{C}$$

The heat capacity of each block is

$$C = mC_\mathrm{s}$$

where C_s is the specific heat capacity

so $\Delta H(\text{individual}) = mC_\mathrm{s}\Delta T = 1.00 \times 10^3\ \mathrm{g} \times 0.449\ \mathrm{J\ K^{-1}\,g^{-1}} \times (\pm 87.\overline{5}\ \mathrm{K}) = \pm 39\ \mathrm{kJ}$

These two enthalpy changes add up to zero: $\boxed{\Delta H_\mathrm{tot} = 0}$

$$\Delta S = mC_\mathrm{s}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right);\quad 200°\mathrm{C} = 473.2\ \mathrm{K};\ 25°\mathrm{C} = 298.2\ \mathrm{K};\ 112.\overline{5}°\mathrm{C} = 385.\overline{7}\ \mathrm{K}$$

$$\Delta S_1 = (1.00 \times 10^3\ \mathrm{g}) \times (0.449\ \mathrm{J\ K^{-1}\,g^{-1}}) \times \ln\left(\frac{385.7}{298.2}\right) = 115.\overline{5}\ \mathrm{J\ K^{-1}}$$

$$\Delta S_2 = (1.00 \times 10^3\ \mathrm{g}) \times (0.449\ \mathrm{J\ K^{-1}\,g^{-1}}) \times \ln\left(\frac{385.7}{473.2}\right) = -91.80\overline{2}\ \mathrm{J\ K^{-1}}$$

$$\Delta S_\mathrm{total} = \Delta S_1 + \Delta S_2 = \boxed{24\ \mathrm{J\ K^{-1}}}$$

E3.6(b) (a) $q = 0$ [adiabatic]

(b) $w = -p_\mathrm{ex}\Delta V = -(1.5\,\mathrm{atm}) \times \left(\dfrac{1.01 \times 10^5\ \mathrm{Pa}}{\mathrm{atm}}\right) \times (100.0\ \mathrm{cm^2}) \times (15\ \mathrm{cm}) \times \left(\dfrac{1\ \mathrm{m^3}}{10^6\ \mathrm{cm^3}}\right)$

$$= -22\overline{7.2}\ \mathrm{J} = \boxed{-230\ \mathrm{J}}$$

(c) $\Delta U = q + w = 0 - 230\ \mathrm{J} = \boxed{-230\ \mathrm{J}}$

(d) $\Delta U = nC_{V,\mathrm{m}}\Delta T$

$$\Delta T = \frac{\Delta U}{nC_{V,\mathrm{m}}} = \frac{-22\overline{7.2}\ \mathrm{J}}{(1.5\ \mathrm{mol}) \times (28.8\ \mathrm{J\ K^{-1}\,mol^{-1}})} = \boxed{-5.3\ \mathrm{K}}$$

(e) Entropy is a state function, so we can compute it by any convenient path. Although the specified transformation is adiabatic, a more convenient path is constant-volume cooling followed by isothermal expansion. The entropy change is the sum of the entropy changes of these two steps:

$$\Delta S = \Delta S_1 + \Delta S_2 = nC_{V,\mathrm{m}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right) + nR\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)\ [3.23\ \&\ 3.17]$$

$$T_\mathrm{f} = 288.\overline{15}\ \mathrm{K} - 5.26\ \mathrm{K} = 282.\overline{9}\ \mathrm{K}$$

$$V_\mathrm{i} = \frac{nRT}{p_\mathrm{i}} = \frac{(1.5\ \mathrm{mol}) \times (8.206 \times 10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (288.\overline{2}\ \mathrm{K})}{9.0\ \mathrm{atm}}$$

$$= 3.9\overline{42}\ \mathrm{dm^3}$$

$$V_\mathrm{f} = 3.9\overline{42}\ \mathrm{dm^3} + (100\ \mathrm{cm^2}) \times (15\ \mathrm{cm}) \times \left(\frac{1\ \mathrm{dm^3}}{1000\ \mathrm{cm^3}}\right)$$

$$= 3.9\overline{42}\ \mathrm{dm^3} + 1.5\ \mathrm{dm^3} = 5.4\overline{4}\ \mathrm{dm^3}$$

$$\Delta S = (1.5\ \mathrm{mol}) \times \left\{(28.8\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{282.\overline{9}}{288.\overline{2}}\right) + (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{5.4\overline{4}}{3.9\overline{42}}\right)\right\}$$

$$= 1.5\ \mathrm{mol}(-0.534\overline{6}\ \mathrm{J\,K^{-1}\,mol^{-1}} + 2.67\overline{8}\ \mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{3.2\ \mathrm{J\,K^{-1}}}$$

E3.7(b) (a) $\Delta_\mathrm{vap}S = \dfrac{\Delta_\mathrm{vap}H}{T_\mathrm{b}} = \dfrac{35.27 \times 10^3\ \mathrm{J\,mol^{-1}}}{(64.1 + 273.15)\ \mathrm{K}} = +104.5\overline{8}\ \mathrm{J\,K^{-1}} = \boxed{104.6\ \mathrm{J\,K^{-1}}}$

(b) If vaporization occurs reversibly, as is generally assumed

$\Delta S_\mathrm{sys} + \Delta S_\mathrm{sur} = 0$ so $\Delta S_\mathrm{sur} = \boxed{-104.6\ \mathrm{J\,K^{-1}}}$

E3.8(b) (a) $\Delta_\mathrm{r}S^\ominus = S_\mathrm{m}^\ominus(\mathrm{Zn^{2+}},\mathrm{aq}) + S_\mathrm{m}^\ominus(\mathrm{Cu},\mathrm{s}) - S_\mathrm{m}^\ominus(\mathrm{Zn},\mathrm{s}) - S_\mathrm{m}^\ominus(\mathrm{Cu^{2+}},\mathrm{aq})$

$= [-112.1 + 33.15 - 41.63 + 99.6]\ \mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{-21.0\ \mathrm{J\,K^{-1}\,mol^{-1}}}$

(b) $\Delta_\mathrm{r}S^\ominus = 12S_\mathrm{m}^\ominus(\mathrm{CO_2},\mathrm{g}) + 11S_\mathrm{m}^\ominus(\mathrm{H_2O},\mathrm{l}) - S_\mathrm{m}^\ominus(\mathrm{C_{12}H_{22}O_{11}},\mathrm{s}) - 12S_\mathrm{m}^\ominus(\mathrm{O_2},\mathrm{g})$

$= [(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14)]\ \mathrm{J\,K^{-1}\,mol^{-1}}$

$= \boxed{+512.0\ \mathrm{J\,K^{-1}\,mol^{-1}}}$

E3.9(b) (a) $\Delta_\mathrm{r}H^\ominus = \Delta_\mathrm{f}H^\ominus(\mathrm{Zn^{2+}},\mathrm{aq}) - \Delta_\mathrm{f}H^\ominus(\mathrm{Cu^{2+}},\mathrm{aq})$

$= -153.89 - 64.77\ \mathrm{kJ\,mol^{-1}} = -218.66\ \mathrm{kJ\,mol^{-1}}$

$\Delta_\mathrm{r}G^\ominus = -218.66\ \mathrm{kJ\,mol^{-1}} - (298.15\ \mathrm{K}) \times (-21.0\ \mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{-212.40\ \mathrm{kJ\,mol^{-1}}}$

(b) $\Delta_\mathrm{r}H^\ominus = \Delta_\mathrm{c}H^\ominus = -5645\ \mathrm{kJ\,mol^{-1}}$

$\Delta_\mathrm{r}G^\ominus = -5645\ \mathrm{kJ\,mol^{-1}} - (298.15\ \mathrm{K}) \times (512.0\ \mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{-5798\ \mathrm{kJ\,mol^{-1}}}$

E3.10(b) (a) $\Delta_\mathrm{r}G^\ominus = \Delta_\mathrm{f}G^\ominus(\mathrm{Zn^{2+}},\mathrm{aq}) - \Delta_\mathrm{f}G^\ominus(\mathrm{Cu^{2+}},\mathrm{aq})$

$= -147.06 - 65.49\ \mathrm{kJ\,mol^{-1}} = \boxed{-212.55\ \mathrm{kJ\,mol^{-1}}}$

(b) $\Delta_\mathrm{r}G^\ominus = 12\Delta_\mathrm{f}G^\ominus(\mathrm{CO_2},\mathrm{g}) + 11\Delta_\mathrm{f}G^\ominus(\mathrm{H_2O},\mathrm{l}) - \Delta_\mathrm{f}G^\ominus(\mathrm{C_{12}H_{22}O_{11}},\mathrm{s}) - 12\Delta_\mathrm{f}G^\ominus(\mathrm{O_2},\mathrm{g})$

$= [12 \times (-394.36) + 11 \times (-237.13) - (-1543) - 12 \times 0]\ \mathrm{kJ\,mol^{-1}}$

$= \boxed{-5798\ \mathrm{kJ\,mol^{-1}}}$

COMMENT. In each case these values of $\Delta_\mathrm{r}G^\ominus$ agree closely with the calculated values in Exercise 3.9(b).

E3.11(b) $\mathrm{CO(g)} + \mathrm{CH_3OH(l)} \rightarrow \mathrm{CH_3COOH(l)}$

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu\Delta_f H^\ominus - \sum_{\text{Reactants}} \nu\Delta_f H^\ominus \;[2.32]$$

$$= -484.5\ \mathrm{kJ\ mol^{-1}} - (-238.66\ \mathrm{kJ\ mol^{-1}}) - (-110.53\ \mathrm{kJ\ mol^{-1}})$$
$$= -135.3\bar{1}\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus \;[3.25a]$$

$$= 159.8\ \mathrm{J\ K^{-1}\ mol^{-1}} - 126.8\ \mathrm{J\ K^{-1}\ mol^{-1}} - 197.67\ \mathrm{J\ K^{-1}\ mol^{-1}}$$
$$= -164.6\bar{7}\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$
$$= -135.3\bar{1}\ \mathrm{kJ\ mol^{-1}} - (298\ \mathrm{K}) \times (-164.6\bar{7}\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$= -135.3\bar{1}\ \mathrm{kJ\ mol^{-1}} + 49.07\bar{2}\ \mathrm{kJ\ mol^{-1}} = \boxed{-86.2\ \mathrm{kJ\ mol^{-1}}}$$

E3.12(b) The formation reaction of urea is

$$\mathrm{C(gr)} + \tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{N_2(g)} + 2\,\mathrm{H_2(g)} \rightarrow \mathrm{CO(NH_2)_2(s)}$$

The combustion reaction is

$$\mathrm{CO(NH_2)_2(s)} + \tfrac{3}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + 2\,\mathrm{H_2O(l)} + \mathrm{N_2(g)}$$

$$\Delta_c H^\ominus = \Delta_f H^\ominus(\mathrm{CO_2,g}) + 2\Delta_f H^\ominus(\mathrm{H_2O,l}) - \Delta_f H^\ominus(\mathrm{CO(NH_2)_2,s})$$

$$\Delta_f H^\ominus(\mathrm{CO(NH_2)_2,s}) = \Delta_f H^\ominus(\mathrm{CO_2,g}) + 2\Delta_f H^\ominus(\mathrm{H_2O,l}) - \Delta_c H^\ominus(\mathrm{CO(NH_2)_2,s})$$
$$= -393.51\ \mathrm{kJ\ mol^{-1}} + (2) \times (-285.83\ \mathrm{kJ\ mol^{-1}}) - (-632\ \mathrm{kJ\ mol^{-1}})$$
$$= -333.17\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f S^\ominus = S_m^\ominus(\mathrm{CO(NH_2)_2,s}) - S_m^\ominus(\mathrm{C,gr}) - \tfrac{1}{2}S_m^\ominus(\mathrm{O_2,g}) - S_m^\ominus(\mathrm{N_2,g}) - 2S_m^\ominus(\mathrm{H_2,g})$$
$$= 104.60\ \mathrm{J\ K^{-1}\ mol^{-1}} - 5.740\ \mathrm{J\ K^{-1}\ mol^{-1}} - \tfrac{1}{2}(205.138\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$-191.61\ \mathrm{J\ K^{-1}\ mol^{-1}} - 2(130.684\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$= -456.68\bar{7}\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$$
$$= -333.1\bar{7}\ \mathrm{kJ\ mol^{-1}} - (298\ \mathrm{K}) \times (-456.68\bar{7}\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$= -333.1\bar{7}\ \mathrm{kJ\ mol^{-1}} + 136.\overline{093}\ \mathrm{kJ\ mol^{-1}}$$
$$= \boxed{-197\ \mathrm{kJ\ mol^{-1}}}$$

E3.13(b) (a) $$\Delta S(\text{gas}) = nR\ln\left(\frac{V_f}{V_i}\right)[3.17] = \left(\frac{21\ \mathrm{g}}{39.95\ \mathrm{g\ mol^{-1}}}\right) \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\frac{4.60}{1.20}$$
$$= 5.8\overline{73}\ \mathrm{J\ K^{-1}} = \boxed{5.9\ \mathrm{J\ K^{-1}}}$$

$\Delta S(\text{surroundings}) = -\Delta S(\text{gas}) = \boxed{-5.9\ \mathrm{J\ K^{-1}}}$ [reversible]

$\Delta S(\text{total}) = \boxed{0}$

(b) $\Delta S(\text{gas}) = \boxed{+5.9\ \mathrm{J\ K^{-1}}}$ [S is a state function]

$\Delta S(\text{surroundings}) = \boxed{0}$ [no change in surroundings]

$$\Delta S(\text{total}) = \boxed{+5.9\ \text{J K}^{-1}}$$

(c) $q_{\text{rev}} = 0$ so $\Delta S(\text{gas}) = \boxed{0}$

$\Delta S(\text{surroundings}) = \boxed{0}$ [no heat is transfered to the surroundings]

$$\Delta S(\text{total}) = \boxed{0}$$

E3.14(b) $C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$

$$\begin{aligned}\Delta_r G^\ominus &= 3\Delta_f G^\ominus(CO_2, g) + 4\Delta_f G^\ominus(H_2O, l) - \Delta_f G^\ominus(C_3H_8, g) - 0\\ &= 3(-394.36\ \text{kJ mol}^{-1}) + 4(-237.13\ \text{kJ mol}^{-1}) - 1(-23.49\ \text{kJ mol}^{-1})\\ &= -2108.11\ \text{kJ mol}^{-1}\end{aligned}$$

The maximum non-expansion work is $\boxed{2108.11\ \text{kJ mol}^{-1}}$ since $|w_{\text{add,max}}| = |\Delta G|$.

E3.15(b) (a) $\eta = 1 - \dfrac{T_c}{T_h}\ [3.10] = 1 - \dfrac{500\ \text{K}}{1000\ \text{K}} = \boxed{0.500}$

(b) Maximum work $= \eta\,|q_h| = (0.500) \times (1.0\ \text{kJ}) = \boxed{0.50\ \text{kJ}}$

(c) $\eta_{\max} = \eta_{\text{rev}}$ and $|w_{\max}| = |q_h| - |q_{c,\min}|$

$$\begin{aligned}|q_{c,\min}| &= |q_h| - |w_{\max}|\\ &= 1.0\ \text{kJ} - 0.50\ \text{kJ} = \boxed{0.5\ \text{kJ}}\end{aligned}$$

E3.16(b) $\Delta G = nRT\ln\left(\dfrac{p_f}{p_i}\right)[3.59] = nRT\ln\left(\dfrac{V_i}{V_f}\right)$ [Boyle's law]

$$\Delta G = (2.5\times10^{-3}\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K}) \times \ln\left(\frac{72}{100}\right) = \boxed{-2.0\ \text{J}}$$

E3.17(b) $\left(\dfrac{\partial G}{\partial T}\right)_p = -S\ [3.53]$; hence $\left(\dfrac{\partial G_f}{\partial T}\right)_p = -S_f$, and $\left(\dfrac{\partial G_i}{\partial T}\right)_p = -S_i$

$$\begin{aligned}\Delta S = S_f - S_i &= -\left(\frac{\partial G_f}{\partial T}\right)_p + \left(\frac{\partial G_i}{\partial T}\right)_p = -\left(\frac{\partial(G_f - G_i)}{\partial T}\right)_p\\ &= -\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\frac{\partial}{\partial T}\left(-73.1\ \text{J} + 42.8\ \text{J} \times \frac{T}{\text{K}}\right)\\ &= \boxed{-42.8\ \text{J K}^{-1}}\end{aligned}$$

E3.18(b) $dG = -SdT + Vdp$ [3.52]; at constant T, $dG = Vdp$, therefore

$$\Delta G = \int_{p_i}^{p_f} V\,dp$$

The change in volume of a condensed phase under isothermal compression is given by the isothermal compressibility (eqn 2.43):

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = 1.26\times10^{-9}\ \text{Pa}^{-1}$$

This small isothermal compressibility (typical of condensed phases) tells us that we can expect a small change in volume from even a large increase in pressure. So we can make the following approximations to obtain a simple expression for the volume as a function of the pressure:

$$\kappa_T \approx -\frac{1}{V}\left(\frac{V-V_\text{i}}{p-p_\text{i}}\right) \approx -\frac{1}{V_\text{i}}\left(\frac{V-V_\text{i}}{p}\right), \quad \text{so} \quad V = V_\text{i}(1-\kappa_T p)$$

where V_i is the volume at 1 atm, namely the sample mass over the density, m/ρ:

$$\Delta G = \int_{100\ \text{kPa}}^{100\ \text{MPa}} \frac{m}{\rho}(1-\kappa_T p)\,\mathrm{d}p$$

$$= \frac{m}{\rho}\left(\int_{100\ \text{kPa}}^{100\ \text{MPa}} \mathrm{d}p - \kappa_T \int_{100\ \text{kPa}}^{100\ \text{MPa}} p\,\mathrm{d}p\right)$$

$$= \frac{m}{\rho}\left(p\Big|_{100\,\text{kPa}}^{100\,\text{MPa}} - \tfrac{1}{2}\kappa_T p^2\Big|_{100\,\text{kPa}}^{100\,\text{MPa}}\right)$$

$$= \frac{25\ \text{g}}{0.791\ \text{g cm}^{-3}}(9.99\times10^{7}\ \text{Pa} - \tfrac{1}{2}(1.26\times10^{-9}\ \text{Pa}^{-1})\times(1.00\times10^{16}\ \text{Pa}^2))$$

$$= 31.\bar{6}\ \text{cm}^3 \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3 \times 9.36\times10^{7}\ \text{Pa}$$

$$= 2.9\bar{6}\times10^{3}\ \text{J} = \boxed{3.0\ \text{kJ}}$$

E3.19(b) $\Delta G_\text{m} = G_\text{m,f} - G_\text{m,i} = RT\ln\left(\frac{p_\text{f}}{p_\text{i}}\right)$ [3.59]

$$= (8.314\ \text{J K}^{-1}\,\text{mol}^{-1})\times(323\,\text{K})\times\ln\left(\frac{252.0}{92.0}\right) = \boxed{2.71\ \text{kJ mol}^{-1}}$$

E3.20(b) For an ideal gas, $G_\text{m}^\circ = G_\text{m}^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)$ [3.59 with $G_\text{m} = G_\text{m}^\circ$]

But for a real gas, $G_\text{m} = G_\text{m}^\ominus + RT\ln\left(\frac{f}{p^\ominus}\right)$ [3.61]

So $G_\text{m} - G_\text{m}^\circ = RT\ln\frac{f}{p}$ [3.61 minus 3.59]; $\frac{f}{p} = \phi$

$$= RT\ln\phi = (8.314\ \text{J K}^{-1}\,\text{mol}^{-1})\times(290\,\text{K})\times(\ln 0.68)$$

$$= \boxed{-0.93\ \text{kJ mol}^{-1}}$$

E3.21(b)

$$\Delta G = nV_{\mathrm{m}}\Delta p\,[3.58] = V\Delta p$$

$$\Delta G = (1.0\ \mathrm{dm^3}) \times \left(\frac{1\mathrm{m^3}}{10^3\,\mathrm{dm^3}}\right) \times (200 \times 10^3\ \mathrm{Pa}) = 200\ \mathrm{Pa\ m^3} = \boxed{200\ \mathrm{J}}$$

E3.22(b)

$$\Delta G_{\mathrm{m}} = RT\ \ln\left(\frac{p_{\mathrm{f}}}{p_{\mathrm{i}}}\right) = (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (500\ \mathrm{K}) \times \ln\left(\frac{100.0\ \mathrm{kPa}}{50.0\ \mathrm{kPa}}\right)$$

$$= \boxed{+2.88\ \mathrm{kJ\ mol^{-1}}}$$

Solutions to problems

Solutions to numerical problems

P3.2

$$\Delta S_{\mathrm{m}} = \int_{T_1}^{T_2} \frac{C_{p,\mathrm{m}}\mathrm{d}T}{T}\,[3.22] = \int_{T_1}^{T_2} \left(\frac{a + bT}{T}\right)\mathrm{d}T = a\ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1)$$

$a = 91.45\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $b = 7.5 \times 10^{-2}\ \mathrm{J\ K^{-2}\ mol^{-1}}$

$$\Delta S_{\mathrm{m}} = (91.47\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln\left(\frac{300\ \mathrm{K}}{273\ \mathrm{K}}\right) + (0.075\ \mathrm{J\ K^{-2}\ mol^{-1}}) \times (27\,\mathrm{K})$$

$$= \boxed{10.\bar{7}\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

P3.4 First, determine the final state in each section. In section B, the volume was halved at constant temperature, so the pressure was doubled: $p_{\mathrm{B,f}} = 2p_{\mathrm{B,i}}$. The piston ensures that the pressures are equal in both chambers, so $p_{\mathrm{A,f}} = 2p_{\mathrm{B,i}} = 2p_{\mathrm{A,i}}$. From the perfect gas law

$$\frac{T_{\mathrm{A,f}}}{T_{\mathrm{A,i}}} = \frac{p_{\mathrm{A,f}}V_{\mathrm{A,f}}}{p_{\mathrm{A,i}}V_{\mathrm{A,i}}} = \frac{(2p_{\mathrm{A,i}}) \times (3.00\ \mathrm{dm^3})}{(p_{\mathrm{A,i}}) \times (2.00\ \mathrm{dm^3})} = 3.00, \quad \text{so} \quad T_{\mathrm{A,f}} = 900\ \mathrm{K}$$

$$\text{(a)}\quad \Delta S_{\mathrm{A}} = nC_{V,\mathrm{m}}\ln\left(\frac{T_{\mathrm{A,f}}}{T_{\mathrm{A,i}}}\right)[3.23] + nR\ln\left(\frac{V_{\mathrm{A,f}}}{V_{\mathrm{A,i}}}\right)[3.17]$$

$$\Delta S_{\mathrm{A}} = (2.0\ \mathrm{mol}) \times (20\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln 3.00$$

$$+ (2.00\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln\left(\frac{3.00\ \mathrm{dm^3}}{2.00\ \mathrm{dm^3}}\right)$$

$$= \boxed{50.7\ \mathrm{J\ K^{-1}}}$$

$$\Delta S_{\mathrm{B}} = nR\ln\left(\frac{V_{\mathrm{B,f}}}{V_{\mathrm{B,i}}}\right) = (2.00\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln\left(\frac{1.00\ \mathrm{dm^3}}{2.00\ \mathrm{dm^3}}\right)$$

$$= \boxed{-11.5\ \mathrm{J\ K^{-1}}}$$

(b) The Helmholtz free energy is defined as $A = U - TS$ [3.33]. Because section B is isothermal, $\Delta U = 0$ and $\Delta(TS) = T\Delta S$, so

$$\Delta A_{\mathrm{B}} = -T_{\mathrm{B}}\Delta S_{\mathrm{B}} = -(300\ \mathrm{K})(-11.5\ \mathrm{J\ K^{-1}}) = 3.46\times10^{3}\ \mathrm{J} = \boxed{+3.46\ \mathrm{kJ}}$$

In section A, we cannot compute $\Delta(TS)$, so we cannot compute ΔU. ΔA $\boxed{\text{is indeterminate}}$ in both magnitude and sign. We know that in a perfect gas, U depends only on temperature; moreover, $U(T)$ is an increasing function of T, for $\dfrac{\partial U}{\partial T} = C$ (heat capacity), which is positive, since $\Delta T > 0$, $\Delta U > 0$ as well. But $\Delta(TS) > 0$ too, since both the temperature and the entropy increase.

(c) Likewise, under constant-temperature conditions

$$\Delta G = \Delta H - T\Delta S$$

In section B, $\Delta H_{\mathrm{B}} = 0$ (constant temperature, perfect gas), so

$$\Delta G_{\mathrm{B}} = -T_{\mathrm{B}}\Delta S_{\mathrm{B}} = -(300\ \mathrm{K})\times(-11.5\ \mathrm{J\ K^{-1}}) = \boxed{3.46\times10^{3}\ \mathrm{J}}$$

ΔG_{A} is $\boxed{\text{indeterminate}}$ in both magnitude and sign.

(d) $\Delta S(\text{total system}) = \Delta S_{\mathrm{A}} + \Delta S_{\mathrm{B}} = (50.7 - 11.5)\ \mathrm{J\ K^{-1}} = \boxed{+39.2\ \mathrm{J\ K^{-1}}}$

If the process has been carried out reversibly as assumed in the statement of the problem we can say

$$\Delta S(\text{system}) = \Delta S(\text{surroundings}) = 0$$

Hence, $\Delta S(\text{surroundings}) = \boxed{-39.2\ \mathrm{J\ K^{-1}}}$

Question. Can you design this process such that heat is added to section A reversibly?

P3.6

	q	w	$\Delta U = \Delta H$	ΔS	ΔS_{sur}	ΔS_{tot}
Path (a)	2.74 kJ	−2.74 kJ	0	9.13 J K⁻¹	−9.13 J K⁻¹	0
Path (b)	1.66 kJ	−1.66 kJ	0	9.13 J K⁻¹	−5.53 J K⁻¹	3.60 J K⁻¹

Path (a)

$$w = -nRT\ln\left(\frac{V_{\mathrm{f}}}{V_{\mathrm{i}}}\right)[2.10] = -nRT\ln\left(\frac{p_{\mathrm{i}}}{p_{\mathrm{f}}}\right)\text{[Boyle's law]}$$

$$= -(1.00\ \mathrm{mol})\times(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(300\ \mathrm{K})\times\ln\left(\frac{3.00\ \mathrm{atm}}{1.00\ \mathrm{atm}}\right) = -2.74\times10^{3}\ \mathrm{J}$$

$$= \boxed{-2.74\ \mathrm{kJ}}$$

$$\Delta H = \Delta U = \boxed{0}\ \text{[isothermal process in perfect gas]}$$

$$q = \Delta U - w = 0 - (-2.74\ \mathrm{kJ}) = \boxed{+2.74\ \mathrm{kJ}}$$

$$\Delta S = \frac{q_{\mathrm{rev}}}{T}\ \text{[isothermal]} = \frac{2.74\times10^{3}\ \mathrm{J}}{300\ \mathrm{K}} = \boxed{+9.13\ \mathrm{J\ K^{-1}}}$$

$$\Delta S_{\text{tot}} = \boxed{0} \text{ [reversible process]}$$

$$\Delta S_{\text{sur}} = \Delta S_{\text{tot}} - \Delta S = 0 - 9.13 \text{ J K}^{-1} = \boxed{-9.13 \text{ J K}^{-1}}$$

Path (*b*)

$$w = -p_{\text{ex}}(V_{\text{f}} - V_{\text{i}}) = -p_{\text{ex}}\left(\frac{nRT}{p_{\text{f}}} - \frac{nRT}{p_{\text{i}}}\right) = -nRT\left(\frac{p_{\text{ex}}}{p_{\text{f}}} - \frac{p_{\text{ex}}}{p_{\text{i}}}\right)$$

$$= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1}) \times (300 \text{ K}) \times \left(\frac{1.00 \text{ atm}}{1.00 \text{ atm}} - \frac{1.00 \text{ atm}}{3.00 \text{ atm}}\right)$$

$$= -1.66 \times 10^3 \text{ J} = \boxed{-1.66 \text{ kJ}}$$

$$\Delta H = \Delta U = \boxed{0} \text{ [isothermal process in perfect gas]}$$

$$q = \Delta U - w = 0 - (-1.66 \text{ kJ}) = \boxed{+1.66 \text{ kJ}}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ [isothermal]} = \frac{2.74 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{+9.13 \text{ J K}^{-1}}$$

Note: One can arrive at this by using q from *Path* (*a*) as the reversible path, or one can simply use ΔS from *Path* (*a*), realizing that entropy is a state function.

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} = \frac{-q}{T_{\text{sur}}} = \frac{-1.66 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{-5.53 \text{ J K}^{-1}}$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}} = (9.13 - 5.53) \text{ J K}^{-1} = \boxed{+3.60 \text{ J K}^{-1}}$$

P3.8 ΔS depends on only the initial and final states, so we can use $\Delta S = nC_{p,\text{m}} \ln \dfrac{T_{\text{f}}}{T_{\text{i}}}$ [3.23].

Since $q = nC_{p,\text{m}}(T_{\text{f}} - T_{\text{i}})$, $T_{\text{f}} = T_{\text{i}} + \dfrac{q}{nC_{p,\text{m}}} = T_{\text{i}} + \dfrac{I^2Rt}{nC_{p,\text{m}}}$ $[q = ItV = I^2Rt]$

That is, $\Delta S = nC_{p,\text{m}} \ln\left(1 + \dfrac{I^2Rt}{nC_{p,\text{m}}T_{\text{i}}}\right)$

Since $n = \dfrac{500 \text{ g}}{63.5 \text{ g mol}^{-1}} = 7.87 \text{ mol}$

$$\Delta S = (7.87 \text{ mol}) \times (24.4 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(1 + \frac{(1.00 \text{ A})^2 \times (1000\ \Omega) \times (15.0 \text{ s})}{(7.87) \times (24.4 \text{ J K}^{-1}) \times (293 \text{ K})}\right)$$

$$= (192 \text{ J K}^{-1}) \times (\ln 1.27) = \boxed{+45.4 \text{ J K}^{-1}}$$

$[1 \text{ J} = 1 \text{ AVs} = 1 \text{ A}^2\,\Omega \text{ s}]$

For the second experiment, no change in state occurs for the copper, hence $\Delta S(\text{copper}) = 0$. However, for the water, considered as a large heat sink

$$\Delta S(\text{water}) = \frac{q}{T} = \frac{I^2Rt}{T} = \frac{(1.00 \text{ A})^2 \times (1000\ \Omega) \times (15.0 \text{ s})}{293 \text{ K}} = \boxed{+51.2 \text{ J K}^{-1}}$$

3.10 Consider the temperature as a function of pressure and enthalpy: $T = T(p,H)$

$$\text{so}\quad \mathrm{d}T = \left(\frac{\partial T}{\partial p}\right)_H \mathrm{d}p + \left(\frac{\partial T}{\partial H}\right)_p \mathrm{d}H$$

The Joule–Thomson expansion is a constant-enthalpy process (Section 2.12). Hence,

$$\mathrm{d}T = \left(\frac{\partial T}{\partial p}\right)_H \mathrm{d}p = \mu \mathrm{d}p$$

$$\begin{aligned}\Delta T &= \int_{p_i}^{p_f} \mu \mathrm{d}p = \mu\Delta p \quad [\mu \text{ is constant}]\\ &= (0.21\ \mathrm{K\ atm^{-1}}) \times (1.00\ \mathrm{atm} - 100\ \mathrm{atm})\\ &= \boxed{-21\ \mathrm{K}}\end{aligned}$$

$$T_f = T_i + \Delta T = (373 - 21)\ \mathrm{K} = 352\ \mathrm{K}\ [\text{Mean } T = 363\ \mathrm{K}]$$

Consider the entropy as a function of temperature and pressure: $S = S(T,p)$.

$$\text{Therefore, } \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad [\text{Table 3.5}]$$

$$\text{For}\quad V_\mathrm{m} = \frac{RT}{p}(1 + Bp)$$

$$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = \frac{R}{p}(1 + Bp)$$

$$\text{Then,}\quad \mathrm{d}S_\mathrm{m} = \frac{C_{p,\mathrm{m}}}{T}\mathrm{d}T - \frac{R}{p}(1 + Bp)\mathrm{d}p$$

$$\text{or}\quad \mathrm{d}S_\mathrm{m} = \frac{C_{p,\mathrm{m}}}{T}\mathrm{d}T - \frac{R}{p}\mathrm{d}p - RB\,\mathrm{d}p$$

On integration

$$\begin{aligned}\Delta S_\mathrm{m} &= \int_1^2 \mathrm{d}S_\mathrm{m} = C_{p,\mathrm{m}}\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{p_2}{p_1}\right) - RB(p_2 - p_1)\\ &= \tfrac{5}{2}R\ln\left(\frac{352}{373}\right) - R\ln\left(\frac{1}{100}\right) - R\left(-\frac{0.525\ \mathrm{atm^{-1}}}{363}\right) \times (-99\ \mathrm{atm})\\ &= \boxed{+35.9\ \mathrm{J\ K^{-1}\ mol^{-1}}}\end{aligned}$$

P3.12 $$\Delta_r H^\ominus = \sum_{\text{products}} \nu\Delta_f H^\ominus - \sum_{\text{reactants}} \nu\Delta_f H^\ominus \text{ [2.34a]}$$

$$\Delta_r H^\ominus(298\text{ K}) = 1\times\Delta_f H^\ominus(\text{CO,g}) + 1\times\Delta_f H^\ominus(\text{H}_2\text{O,g}) - 1\times\Delta_f H^\ominus(\text{CO}_2\text{,g})$$

$$= \{-110.53 - 241.82 - (-393.51)\}\text{ kJ mol}^{-1} = \boxed{+41.16\text{ kJ mol}^{-1}}$$

$$\Delta_r S^\ominus = \sum_{\text{products}} \nu S_m^\ominus - \sum_{\text{reactants}} \nu S_m^\ominus \text{ [3.25a]}$$

$$\Delta_r S^\ominus(298\text{ K}) = 1\times S_m^\ominus(\text{CO,g}) + 1\times S_m^\ominus(\text{H}_2\text{O,g}) - 1\times S_m^\ominus(\text{CO}_2\text{,g}) - 1\times S_m^\ominus(\text{H}_2\text{,g})$$

$$= (197.67 + 188.83 - 213.74 - 130.684)\text{ kJ mol}^{-1} = \boxed{+42.08\text{ J K}^{-1}\text{ mol}^{-1}}$$

$$\Delta_r H^\ominus(398\text{ K}) = \Delta_r H^\ominus(298\text{ K}) + \int_{298\text{ K}}^{398\text{ K}} \Delta_r C_p^\ominus \mathrm{d}T \text{ [2.36a]}$$

$$= \Delta_r H^\ominus(298\text{ K}) + \Delta_r C_p^\ominus \Delta T \quad \text{[heat capacities constant]}$$

$$\Delta_r C_p^\ominus = 1\times C_{p,m}^\ominus(\text{CO,g}) + 1\times C_{p,m}^\ominus(\text{H}_2\text{O,g}) - 1\times C_{p,m}^\ominus(\text{CO}_2\text{,g}) - 1\times C_{p,m}^\ominus(\text{H}_2\text{,g})$$
$$= (29.14 + 33.58 - 37.11 - 28.824)\text{ J K}^{-1}\text{ mol}^{-1} = -3.21\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_r H^\ominus(398\text{ K}) = (41.16\text{ kJ mol}^{-1}) + (-3.21\text{ J K}^{-1}\text{ mol}^{-1})\times(100\text{ K}) = \boxed{+40.84\text{ kJ mol}^{-1}}$$

For each substance in the reaction

$$\Delta S_m = C_{p,m}\ln\left(\frac{T_f}{T_i}\right) = C_{p,m}\ln\left(\frac{398\text{ K}}{298\text{ K}}\right) \text{ [3.23]}$$

Thus,

$$\Delta_r S^\ominus(398\text{ K}) = \Delta_r S^\ominus(298\text{ K}) + \sum_{\text{products}} \nu C_{p,m}^\ominus \ln\left(\frac{T_f}{T_i}\right) - \sum_{\text{reactants}} \nu C_{p,m}^\ominus(\text{J})\ln\left(\frac{T_f}{T_i}\right)$$

$$= \Delta_r S^\ominus(298\text{K}) + \Delta_r C_p^\ominus \ln\left(\frac{398\text{ K}}{298\text{ K}}\right)$$

$$= (42.08\text{ J K}^{-1}\text{ mol}^{-1}) + (-3.21\text{ J K}^{-1}\text{ mol}^{-1})\ln\left(\frac{398\text{ K}}{298\text{ K}}\right)$$

$$= (42.08 - 0.93)\text{ J K}^{-1}\text{ mol}^{-1} = \boxed{+41.15\text{ J K}^{-1}\text{ mol}^{-1}}$$

COMMENT. Both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ changed little over 100 K for this reaction. This is not an uncommon result.

P3.14 Draw up the following table and proceed as in Problem 3.11.

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$(C_{p,m}/T)$(J K^{-2} mol^{-1})	0.671	0.778	0.908	1.045	1.063	1.024

T/K	100.90	140.86	183.59	225.10	262.99	298.06
$(C_{p,m}/T)$(J K^{-2} mol^{-1})	0.942	0.861	0.787	0.727	0.685	0.659

Plot $C_{p,\mathrm{m}}$ against T (Figure 3.2(a)) and $C_{p,\mathrm{m}}/T$ against T (Figure 3.2(b)), extrapolating to $T = 0$ with $C_{p,\mathrm{m}} = aT^3$ fitted at $T = 14.14$ K, which gives $a = 3.36$ mJ K^{-1} mol^{-1}. Integration by determining the area under the curve then gives

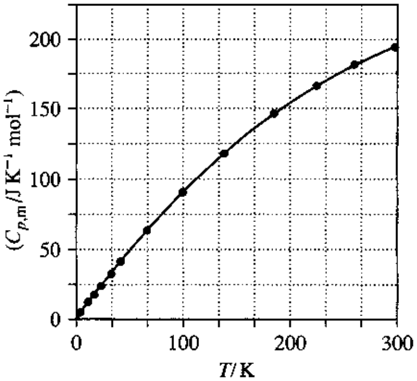


Figure 3.2(a)

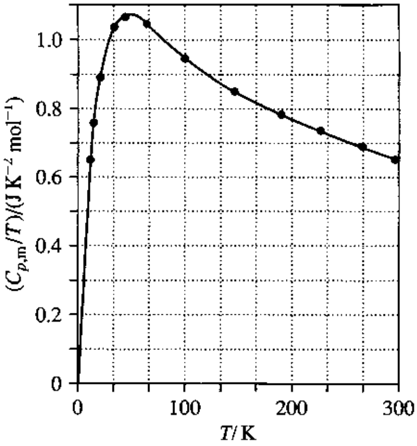


Figure 3.2(b)

$$H_\mathrm{m}^\ominus(298\ \mathrm{K}) - H_\mathrm{m}^\ominus(0) = \int_0^{298\ \mathrm{K}} C_{p,\mathrm{m}}\,\mathrm{d}T = \boxed{34.4\ \mathrm{kJ\ mol^{-1}}}$$

$$S_\mathrm{m}(298\ \mathrm{K}) = S_\mathrm{m}(0) + \int_0^{298\ \mathrm{K}} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T = S_\mathrm{m}(0) + \boxed{243\ \mathrm{J\ K^{-1}\,mol^{-1}}}$$

P3.16 The Gibbs–Helmholtz equation [3.55] may be recast into an analogous equation involving ΔG and ΔH, since

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \left(\frac{\partial G_\mathrm{f}}{\partial T}\right)_p - \left(\frac{\partial G_\mathrm{i}}{\partial T}\right)_p$$

and $\Delta H = H_\mathrm{f} - H_\mathrm{i}$

Thus, $\left(\dfrac{\partial}{\partial T}\dfrac{\Delta_r G^\ominus}{T}\right)_p = -\dfrac{\Delta_r H^\ominus}{T^2}$

$$\mathrm{d}\left(\frac{\Delta_r G^\ominus}{T}\right) = \left(\frac{\partial}{\partial T}\frac{\Delta_r G^\ominus}{T}\right)_p \mathrm{d}T \text{ [constant pressure]} = -\frac{\Delta_r H^\ominus}{T^2}\,\mathrm{d}T$$

$$\Delta\left(\frac{\Delta_r G^\ominus}{T}\right) = -\int_{T_c}^{T} \frac{\Delta_r H^\ominus\,\mathrm{d}T}{T^2}$$

$$\approx -\Delta_r H^\ominus \int_{T_c}^{T} \frac{\mathrm{d}T}{T^2} = \Delta_r H^\ominus\left(\frac{1}{T}-\frac{1}{T_c}\right) \quad [\Delta_r H^\ominus \text{ assumed constant}]$$

Therefore, $\dfrac{\Delta_r G^\ominus(T)}{T} - \dfrac{\Delta_r G^\ominus(T_c)}{T_c} \approx \Delta_r H^\ominus\left(\dfrac{1}{T}-\dfrac{1}{T_c}\right)$

and so $\Delta_r G^\ominus(T) = \dfrac{T}{T_c}\Delta_r G^\ominus(T_c) + \left(1-\dfrac{T}{T_c}\right)\Delta_r H^\ominus(T_c)$

$$= \tau\Delta_r G^\ominus(T_c) + (1-\tau)\Delta_r H^\ominus(T_c), \quad \text{where} \quad \tau = \frac{T}{T_c}$$

For the reaction

$$2\,\mathrm{CO(g)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)}$$

$$\begin{aligned}\Delta_r G^\ominus(T_c) &= 2\Delta_f G^\ominus(\mathrm{CO_2,g}) - 2\Delta_f G^\ominus(\mathrm{CO,g})\\ &= [2\times(-394.36) - 2\times(-137.17)]\ \mathrm{kJ\,mol^{-1}} = -514.38\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus(T_c) &= 2\Delta_f H^\ominus(\mathrm{CO_2,g}) - 2\Delta_f H^\ominus(\mathrm{CO,g})\\ &= [2\times(-393.51) - 2\times(-110.53)]\ \mathrm{kJ\,mol^{-1}} = -565.96\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Therefore, since $\tau = \dfrac{375}{298.15} = 1.25\overline{8}$

$$\begin{aligned}\Delta_r G^\ominus(375\ \mathrm{K}) &= \{(1.25\overline{8})\times(-514.38) + (1-1.25\overline{8})\times(-565.96)\}\ \mathrm{kJ\,mol^{-1}}\\ &= \boxed{-501\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

P3.18 A graphical integration of $\ln\phi = \int_0^p \left(\dfrac{Z-1}{p}\right)\mathrm{d}p$ [3.63] is performed. We draw up the following table:

p/atm	1	4	7	10	40	70	100
$10^3\left(\dfrac{Z-1}{p}\right)\Big/\mathrm{atm^{-1}}$	−2.9	−3.01	−3.03	−3.04	−3.17	−3.19	−3.13

The points are plotted in Figure 3.3. The integral is the shaded area up to zero on the vertical axis, which has the value −0.313, so at 100 atm

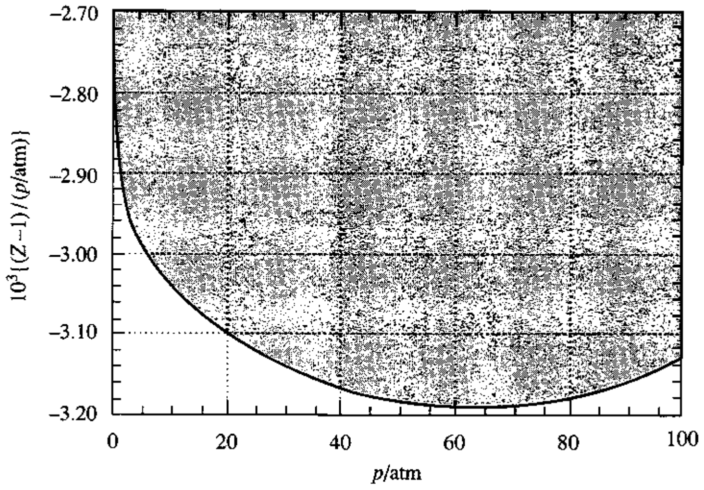


Figure 3.3

$$\phi = e^{-0.313} = 0.73$$

and the fugacity of oxygen is 100 atm × 0.73 = $\boxed{73\ \text{atm}}$.

Solutions to theoretical problems

P3.20 Paths A and B in Figure 3.4 are the reversible adiabatic paths that are assumed to cross at state 1. Path C (dashed) is an isothermal path which connects the adiabatic paths at states 2 and 3. Now go round the cycle (1 → 2, step 1; 1 → 3, step 2; 3 → 1, step 3).

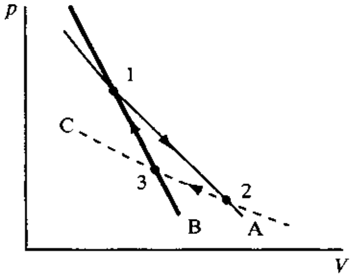


Figure 3.4

Step 1 $\Delta U_1 = q_1 + w_1 = w_1$ [$q_1 = 0$, adiabatic]

Step 2

$\Delta U_2 = q_2 + w_2 = 0$ [isothermal step, energy depends on temperature only]

Step 3 $\Delta U_3 = q_3 + w_3 = w_3$ [$q_3 = 0$, adiabatic]

For the cycle $\Delta U = 0 = w_1 + q_2 + w_2 + w_3$ or $w(\text{net}) = w_1 + w_2 + w_3 = -q_2$

But, $\Delta U_1 = -\Delta U_3$ [$\Delta T_1 = -\Delta T_2$]; hence, $w_1 = -w_3$ and $w(\text{net}) = w_2 = -q_2$, or $-w(\text{net}) = q_2$

Thus, a net amount of work has been done by the system from heat obtained from a heat reservoir at the temperature of step 2, without at the same time transferring heat from a hot to a cold reservoir. This violates the Kelvin statement of the second law. Therefore, the assumption that the two adiabatic reversible paths may intersect is disproven.

Question. May any adiabatic paths intersect, reversible or not?

Alternative solution not requiring the system to be a perfect gas

Note that step 2 above effectively requires the system to be a perfect gas. The following solution is more general.

Suppose that two adiabats cross at point 1.

Consider the isotherm at T crossing both adiabats at points 2 and 3.

We now can define a quasi-steady closed cycle along the two adiabats and the isotherm.

By definition of state variables:

$$\Delta U = \oint dU = 0$$

$$\Delta S = \oint dS = 0$$

Using the first law:

$$\Delta U = \oint dq + \oint dw = q + w$$

$$\Rightarrow q = -w$$

and the second law for reversible processes we have:

$$\Delta S = \oint \frac{dq}{T} = \frac{q}{T}$$

$$\Rightarrow q = 0$$

As T is finite we find:

$$w = -q = 0$$

As the work corresponds to the surface area of our closed cycle we conclude that the two adiabats coincide (are a single curve).

P3.22 $$V = \left(\frac{\partial G}{\partial p}\right)_T [3.53] = \boxed{\frac{RT}{p} + B + Cp + Dp^2}$$

which is the virial equation of state.

P3.24 We start from the fundamental relationship

$$dU = TdS - pdV\,[3.46]$$

But, since $U = U(S,V)$, we may also write

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

Comparing the two expressions, we see that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

These relationships are true in general and hence hold for the perfect gas. We can demonstrate this more explicitly for the perfect gas as follows. For the perfect gas at constant volume

$$\mathrm{d}U = C_V\,\mathrm{d}T$$

and

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \frac{C_V\,\mathrm{d}T}{T}$$

Then, $\left(\frac{\mathrm{d}U}{\mathrm{d}S}\right)_V = \left(\frac{\partial U}{\partial S}\right)_V = \frac{C_V\mathrm{d}T}{\left(\frac{C_V\mathrm{d}T}{T}\right)} = T$

For a reversible adiabatic (constant-entropy) change in a perfect gas

$$\mathrm{d}U = \mathrm{d}w = -p\mathrm{d}V$$

Therefore, $\left(\frac{\partial U}{\partial V}\right)_S = -p$

P3.26 $$\alpha = \left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial T}\right)_p \ [2.42]; \quad \kappa_T = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_T \ [2.43]$$

(a) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ [Maxwell relationship]

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \ \text{[Euler chain relation MB2.3c]}$$

$$= -\frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \ \text{[reciprocal identity, MB2.3b]}$$

$$= -\frac{\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T} = \boxed{+\frac{\alpha}{\kappa_T}}$$

$$\left(\frac{\partial V}{\partial S}\right)_p=\left(\frac{\partial T}{\partial p}\right)_S \text{ [Maxwell relationship]}$$

$$\left(\frac{\partial T}{\partial p}\right)_S=-\left(\frac{\partial T}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_T \text{ [Euler chain]}=-\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}\text{ [reciprocal]}$$

First, treat the numerator:

$$\left(\frac{\partial S}{\partial p}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_p \text{ [Maxwell relation]}=-\alpha V$$

As for the denominator, at constant p

$$\mathrm{d}S=\left(\frac{\partial S}{\partial T}\right)_p\mathrm{d}T \quad\text{and}\quad \mathrm{d}S=\frac{\mathrm{d}q_{\mathrm{rev}}}{T}=\frac{\mathrm{d}H}{T}=\frac{C_p\,\mathrm{d}T}{T}\;[\mathrm{d}q_p=\mathrm{d}H]$$

$$\text{Therefore, }\left(\frac{\partial S}{\partial T}\right)_p=\frac{C_p}{T}\quad\text{and}\quad\left(\frac{\partial V}{\partial S}\right)_p=\boxed{\frac{\alpha TV}{C_p}}$$

(b) $$\left(\frac{\partial p}{\partial S}\right)_V=-\left(\frac{\partial T}{\partial V}\right)_S \text{ [Maxwell relationship]}$$

$$-\left(\frac{\partial T}{\partial V}\right)_S=\frac{1}{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial V}{\partial S}\right)_T}\text{ [Euler chain]}=\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V}\text{ [reciprocal]}$$

$$=\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial U}\right)_V\left(\frac{\partial U}{\partial T}\right)_V}\text{ [Maxwell relation]}=\frac{-\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial U}\right)_V\left(\frac{\partial U}{\partial T}\right)_V}\text{ [Euler chain]}$$

$$=\frac{-\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial U}{\partial T}\right)_V}\text{ [reciprocal identity, twice]}=\boxed{\frac{\alpha T}{\kappa_T C_V}}\left[\left(\frac{\partial U}{\partial S}\right)_V=T\right]$$

P3.28 First use an identity of partial derivatives that involves a change of variable

$$\left(\frac{\partial H}{\partial p}\right)_T=\left(\frac{\partial H}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_T+\left(\frac{\partial H}{\partial p}\right)_S \text{ [MB2.3a]}$$

We will be able to identify some of these terms if we examine an expression for dH analogous to the fundamental equation [3.46]. From the definition of enthalpy, we have:

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S - p\,\mathrm{d}V\,[3.46] + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S + V\,\mathrm{d}p$$

Compare this expression to the exact differential of H considered as a function of S and p:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p$$

Thus, $\left(\frac{\partial H}{\partial S}\right)_p = T,\ \left(\frac{\partial H}{\partial p}\right)_S = V$ [dH exact]

Substitution yields $\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = \boxed{-T\left(\frac{\partial V}{\partial T}\right)_p + V}$ [Maxwell relation]

(a) For $pV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}, \quad \text{hence} \quad \left(\frac{\partial H}{\partial p}\right)_T = \frac{-nRT}{p} + V = \boxed{0}$$

(b) For $p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ [Table 1.7]

Because we cannot express V in closed form as a function of T, we solve for T as a function of V and evaluate

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V = \frac{-T}{\left(\frac{\partial T}{\partial V}\right)_p} + V \text{ [reciprocal identity]}$$

$$T = \frac{p(V - nb)}{nR} + \frac{na(V - nb)}{RV^2}$$

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V - nb)}{RV^3}$$

Therefore, $\left(\frac{\partial H}{\partial p}\right)_T = \frac{-T}{\frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V - nb)}{RV^3}} + V$

which yields after algebraic manipulation

$$\left(\frac{\partial H}{\partial p}\right)_T = \boxed{\frac{nb - \left(\frac{2na}{RT}\right)\lambda^2}{1 - \left(\frac{2na}{RTV}\right)\lambda^2}, \quad \lambda = 1 - \frac{nb}{V}}$$

When $\frac{b}{V_{\mathrm{m}}} \ll 1$, $\lambda \approx 1$ and

$$\frac{2na}{RTV}=\frac{2na}{RT}\times\frac{1}{V}\approx\frac{2na}{RT}\times\frac{p}{nRT}=\frac{2pa}{R^2T^2}$$

Therefore, $\left(\frac{\partial H}{\partial p}\right)_T\approx\frac{nb-\left(\frac{2na}{RT}\right)}{1-\left(\frac{2pa}{R^2T^2}\right)}$

For argon, $a = 1.337\ \mathrm{dm^6\,atm\,mol^{-2}}$, $b = 3.20\times10^{-2}\ \mathrm{dm^3\,mol^{-1}}$,

$$\frac{2na}{RT}=\frac{(2)\times(1.0\ \mathrm{mol})\times(1.337\ \mathrm{dm^6\,atm\,mol^{-2}})}{(8.206\times10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}=0.11\ \mathrm{dm^3}$$

$$\frac{2pa}{R^2T^2}=\frac{(2)\times(10.0\ \mathrm{atm})\times(1.337\ \mathrm{dm^6\,atm\,mol^{-2}})}{[(8.206\times10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})]^2}=0.045$$

Hence, $\left(\frac{\partial H}{\partial p}\right)_T\approx\frac{\{(3.20\times10^{-2})-(0.11)\}\mathrm{dm^3}}{1-0.045}=-0.0832\ \mathrm{dm^3}=\boxed{-8.4\ \mathrm{J\,atm^{-1}}}$

$$\Delta H\approx\left(\frac{\partial H}{\partial p}\right)_T\Delta p\approx(-8.4\ \mathrm{J\,atm^{-1}})\times(1\ \mathrm{atm})=\boxed{-8\ \mathrm{J}}$$

P3.30 $\mu_J=\left(\frac{\partial T}{\partial V}\right)_U\quad C_V=\left(\frac{\partial U}{\partial T}\right)_V$

$$\mu_J C_V=\left(\frac{\partial T}{\partial V}\right)_U\left(\frac{\partial U}{\partial T}\right)_V=\frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T}\text{[Euler chain relation]}$$

$$=-\left(\frac{\partial U}{\partial V}\right)_T\text{[reciprocal identity]}=p-T\left(\frac{\partial p}{\partial T}\right)_V\ [3.51]$$

$$\left(\frac{\partial p}{\partial T}\right)_V=\frac{-1}{\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T}\text{[Euler chain]}=\frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}=\frac{\alpha}{\kappa_T}$$

Therefore, $\boxed{\mu_J C_V=p-\frac{\alpha T}{\kappa_T}}$

P3.32 $\kappa_S=-\left(\frac{1}{V}\right)\times\left(\frac{\partial V}{\partial p}\right)_S=-\frac{1}{V\left(\frac{\partial p}{\partial V}\right)_S}$

The only constant-entropy changes of state for a perfect gas are reversible adiabatic changes, for which

$pV^{\gamma}=\text{const}$

Then, $\left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\frac{\text{const}}{V^\gamma}\right)_S = -\gamma \times \left(\frac{\text{const}}{V^{\gamma+1}}\right) = \frac{-\gamma p}{V}$

Therefore, $\kappa_S = \frac{-1}{V\left(\frac{-\gamma p}{V}\right)} = \frac{+1}{\gamma p}$

Hence, $\boxed{p\gamma\kappa_S = +1}$

3.34 The starting point for the calculation is eqn 3.63. To evaluate the integral, we need an analytical expression for Z, which can be obtained from the equation of state.

(a) We saw in Section 1.4 that the van der Waals coefficient a represents the attractions between molecules, so it may be set equal to zero in this calculation. When we neglect a in the van der Waals equation, that equation becomes

$$p = \frac{RT}{V_\text{m} - b}$$

and hence

$$Z = 1 + \frac{bp}{RT}$$

The integral in eqn 3.63 that we require is therefore

$$\ln\phi = \int_0^p \left(\frac{Z-1}{p}\right)\text{d}p = \int_0^p \left(\frac{b}{RT}\right)\text{d}p = \frac{bp}{RT}$$

Consequently, from eqns 3.62 and 3.63, the fugacity at the pressure p is

$$f = \boxed{pe^{bp/RT}}$$

From Table 1.6, $b = 3.71 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}$, so $pb/RT = 1.516 \times 10^{-2}$, giving

$$f = (10.00\ \text{atm}) \times e^{0.01516} = \boxed{10.2\ \text{atm}}$$

COMMENT. The effect of the repulsive term (as represented by the coefficient b in the van der Waals equation) is to increase the fugacity above the pressure, and so the effective pressure of the gas—its 'escaping tendency'—is greater than if it were perfect.

(b) When we neglect b in the van der Waals equation we have

$$p = \frac{RT}{V_\text{m}} - \frac{a}{V_\text{m}^2}$$

and hence

$$Z = 1 - \frac{a}{RTV_\text{m}}$$

Then, substituting into eqn 3.63 we get

$$\ln\phi = \int_o^p \left(\frac{Z-1}{p}\right)\text{d}p = \int_o^p \frac{-a}{pRTV_\text{m}}\text{d}p$$

In order to perform this integration we must eliminate the variable V_m by solving for it in terms of p. Rewriting the expression for p in the form of a quadratic we have

$$V_m^2 - \frac{RT}{p}V_m + \frac{a}{p} = 0$$

The solution is

$$V_m = \frac{1}{2}\left(\frac{RT}{p} \pm \frac{1}{p}\sqrt{(RT)^2 - 4ap}\right)$$

Applying the approximation $(RT)^2 \gg 4ap$ we obtain

$$V_m = \frac{1}{2}\left(\frac{RT}{p} \pm \frac{RT}{p}\right)$$

Choosing the + sign we get

$V_m = \dfrac{RT}{p}$, which is the perfect-gas volume.

Then,

$$\ln\phi = \int_o^p -\frac{a}{(RT)^2}\mathrm{d}p = \boxed{-\frac{ap}{(RT)^2}}$$

For ammonia, $a = 4.169 \text{ atm dm}^6 \text{ mol}^{-2}$

$$\ln\phi = -\frac{4.169 \text{ atm dm}^6 \text{ mol}^{-2} \times 10.00 \text{ atm}}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})^2}$$

$$= -0.06965$$

$$\phi = 0.9327 = \frac{f}{p}$$

$$f = \phi p = 0.9327 \times 10.00 \text{ atm} = \boxed{9.327 \text{ atm}}$$

Solutions to applications

P3.36 Taking the hint, we have

$$\Delta_{\text{trs}}S^{\ominus}(25°\text{C}) = \Delta S_{\text{i}} + \Delta S_{\text{ii}} + \Delta S_{\text{iii}}$$

We are not given the heat capacity of either the folded or unfolded protein, but if we let $C_{p,m}$ be the heat capacity of the folded protein, the heat capacity of the unfolded protein is $C_{p,m} + 6.28 \text{ kJ K}^{-1} \text{ mol}^{-1}$. So, for the heating and cooling steps, we have:

$$\Delta S_{\text{i}} = C_p \ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) = C_{p,m}\ln\left(\frac{348.7 \text{ K}}{298.2 \text{ K}}\right) \quad [3.23]$$

and $\Delta S_{\text{iii}} = (C_{p,\text{m}} + 6.28\ \text{kJ K}^{-1}\,\text{mol}^{-1})\ln\left(\dfrac{298.2\ \text{K}}{348.7\ \text{K}}\right)$, so

$$\Delta S_{\text{i}} + \Delta S_{\text{iii}} = C_{p,\text{m}}\ln\left(\frac{348.7\ \text{K}}{298.2\ \text{K}}\right) + (C_{p,\text{m}} + 6.28\ \text{kJ K}^{-1}\,\text{mol}^{-1})\ln\left(\frac{298.2\ \text{K}}{348.7\ \text{K}}\right)$$

$$= (6.28\ \text{kJ K}^{-1}\,\text{mol}^{-1})\ln\left(\frac{298.2\ \text{K}}{348.7\ \text{K}}\right) = -0.983\ \text{kJ K}^{-1}\,\text{mol}^{-1}$$

For the transition itself, use Trouton's rule (eqn 3.20):

$$\Delta S_{\text{ii}} = \frac{\Delta_{\text{trs}}H^{\ominus}}{T_{\text{trs}}} = \frac{509\ \text{kJ mol}^{-1}}{348.2\ \text{K}} = 1.46\overline{0}\ \text{kJ K}^{-1}\,\text{mol}^{-1}$$

Hence, $\Delta_{\text{trs}}S^{\ominus} = (1.46\overline{0} - 0.983)\ \text{kJ K}^{-1}\,\text{mol}^{-1} = 0.47\overline{7}\ \text{kJ K}^{-1}\,\text{mol}^{-1} = \boxed{47\overline{7}\ \text{J K}^{-1}\,\text{mol}^{-1}}$

P3.38 (a) At constant temperature,

$$\Delta_{\text{r}}G = \Delta_{\text{r}}H - T\Delta_{\text{r}}S \quad \text{so} \quad \Delta_{\text{r}}S = \frac{\Delta_{\text{r}}H - \Delta_{\text{r}}G}{T}$$

and $\Delta_{\text{r}}S = \dfrac{[-20-(-31)]\ \text{kJ mol}^{-1}}{310\ \text{K}} = +0.035\ \text{kJ K}^{-1}\,\text{mol}^{-1} = \boxed{+35\ \text{J K}^{-1}\,\text{mol}^{-1}}$

The positive sign for the entropy of reaction is consistent with the formation of two new substances, resulting in greater disorder on the product side.

(b) The power density P is

$$P = \frac{|\Delta_{\text{r}}G|n}{V}$$

where n is the number of moles of ATP hydrolysed per second

$$n = \frac{N}{N_{\text{A}}} = \frac{10^{6}\ \text{s}^{-1}}{6.02\times 10^{23}\ \text{mol}^{-1}} = 1.6\overline{6}\times 10^{-18}\ \text{mol s}^{-1}$$

and V is the volume of the cell

$$V = \tfrac{4}{3}\pi r^{3} = \tfrac{4}{3}\pi(10\times 10^{-6}\ \text{m})^{3} = 4.1\overline{9}\times 10^{-15}\ \text{m}^{3}$$

Thus $P = \dfrac{|\Delta_{\text{r}}G|n}{V} = \dfrac{(31\times 10^{3}\ \text{J mol}^{-1})\times(1.6\overline{6}\times 10^{-18}\ \text{mol s}^{-1})}{4.1\overline{9}\times 10^{-15}\ \text{m}^{3}} = \boxed{12\ \text{W m}^{-3}}$

This is orders of magnitude less than the power density of a computer battery, which is about

$$P_{\text{battery}} = \frac{15\ \text{W}}{100\ \text{cm}^{3}}\times\left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^{3} = \boxed{1.5\times 10^{5}\ \text{W m}^{-3}}$$

(c) Simply make a ratio of the magnitudes of the free energies

$$\frac{14.2\ \text{kJ (mol glutamine)}^{-1}}{31\ \text{kJ (mol ATP)}^{-1}} = \boxed{0.46\frac{\text{mol ATP}}{\text{mol glutamine}}}$$

P3.40 The Gibbs–Helmholtz equation is

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)=-\frac{\Delta H}{T^2}$$

so $\displaystyle\int \mathrm{d}\frac{\Delta_r G^\ominus}{T}=-\int\frac{\Delta_r H^\ominus \mathrm{d}T}{T^2}$ and $\displaystyle\frac{\Delta_r G^\ominus_{190}}{T_{190}}=\frac{\Delta_r G^\ominus_{220}}{T_{220}}+\Delta_r H^\ominus\left(\frac{1}{T_{190}}-\frac{1}{T_{220}}\right)$

$$\Delta_r G^\ominus_{190}=\Delta_r G^\ominus_{220}\frac{T_{190}}{T_{220}}+\Delta_r H^\ominus\left(1-\frac{T_{190}}{T_{220}}\right)$$

For the monohydrate

$$\Delta_r G^\ominus_{190}=(46.2\ \mathrm{kJ\ mol^{-1}})\times\left(\frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right)+(127\ \mathrm{kJ\ mol^{-1}})\times\left(1-\frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right),$$

$$\Delta_r G^\ominus_{190}=\boxed{57.2\ \mathrm{kJ\ mol^{-1}}}$$

For the dihydrate

$$\Delta_r G^\ominus_{190}=(69.4\ \mathrm{kJ\ mol^{-1}})\times\left(\frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right)+(188\ \mathrm{kJ\ mol^{-1}})\times\left(1-\frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right),$$

$$\Delta_r G^\ominus_{190}=\boxed{85.6\ \mathrm{kJ\ mol^{-1}}}$$

For the trihydrate

$$\Delta_r G^\ominus_{190}=(93.2\ \mathrm{kJ\ mol^{-1}})\times\left(\frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right)+(237\ \mathrm{kJ\ mol^{-1}})\times\left(1-\frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right),$$

$$\Delta_r G^\ominus_{190}=\boxed{112.8\ \mathrm{kJ\ mol^{-1}}}$$

P3.42 In effect, we are asked to compute the maximum work extractable from a gallon of octane, assuming that the internal combustion engine is a reversible heat engine operating between the specified temperatures, and to equate that quantity of energy with gravitational potential energy of a 1000-kg mass. The efficiency is

$$\eta=\frac{|w|}{|q_\mathrm{h}|}[3.8]=\frac{|w|}{|\Delta H|}=\eta_\mathrm{rev}=1-\frac{T_\mathrm{c}}{T_\mathrm{h}}\ [3.10],\quad \text{so}\quad |w|=|\Delta H|\left(1-\frac{T_\mathrm{c}}{T_\mathrm{h}}\right)$$

$$|\Delta H|=5512\times10^3\ \mathrm{J\ mol^{-1}}\times1.00\ \mathrm{gal}\times\frac{3.00\times10^3\ \mathrm{g}}{1\ \mathrm{gal}}\times\frac{1\ \mathrm{mol}}{114.23\ \mathrm{g}}=1.44\overline{8}\times10^8\ \mathrm{J}$$

$$\text{so}\quad |w|=1.44\overline{8}\times10^8\ \mathrm{J}\times\left(1-\frac{1073\ \mathrm{K}}{2273\ \mathrm{K}}\right)=7.64\overline{2}\times10^7\ \mathrm{J}$$

If this work is converted completely to potential energy, it could lift a 1000-kg object to a height h given by $|w|=mgh$, so

$$h=\frac{|w|}{mg}=\frac{7.64\bar{2}\times10^{7}\ \text{J}}{(1000\ \text{kg})(9.81\ \text{m s}^{-2})}=7.79\times10^{3}\ \text{m}=\boxed{7.79\ \text{km}}$$

3.44 (a) As suggested, relate the work to the temperature-dependent coefficient of performance [*Impact I3.1*]:

$$|\text{d}w|=\frac{|\text{d}q_\text{c}|}{c}=\frac{|C_p\text{d}T|}{\left(\dfrac{T}{T_\text{h}-T}\right)}=C_p\left|\frac{T_\text{h}\text{d}T}{T}-\text{d}T\right|$$

Integrating yields

$$|w|=C_p\left|T_\text{h}\int_{T_\text{i}}^{T_\text{f}}\frac{\text{d}T}{T}-\int_{T_\text{i}}^{T_\text{f}}\text{d}T\right|=C_p\left|T_\text{h}\ln\frac{T_\text{f}}{T_\text{i}}-(T_\text{f}-T_\text{i})\right|=C_p\left(T_\text{h}\ln\frac{T_\text{i}}{T_\text{f}}-T_\text{i}+T_\text{f}\right)$$

(b) The heat capacity is $C_p=(4.184\ \text{J K}^{-1}\ \text{g}^{-1})\times(250\ \text{g})=1046\ \text{J K}^{-1}$, so the work associated with cooling the water from 293 K to the freezing temperature is

$$|w|_\text{cooling}=1046\ \text{J K}^{-1}\times\left(293\ \text{K}\times\ln\frac{293\ \text{K}}{273\ \text{K}}-293\ \text{K}+273\ \text{K}\right)=748\ \text{J}$$

The refrigerator must also remove the heat of fusion at the freezing temperature. For this isothermal process, the coefficient of performance does not change, so

$$|w|_\text{freeze}=\frac{|q_\text{c}|}{c}=\frac{\Delta_\text{fus}H}{\left(\dfrac{T_\text{c}}{T_\text{h}-T_\text{c}}\right)}=\Delta_\text{fus}H\left(\frac{T_\text{h}-T_\text{c}}{T_\text{c}}\right)$$

$$=6.008\times10^{3}\ \text{J mol}^{-1}\times\frac{250\ \text{g}}{18.0\ \text{g mol}^{-1}}\times\left(\frac{293-273}{273}\right)=611\bar{3}\ \text{J}$$

The total work is

$$|w|_\text{total}=|w|_\text{cooling}+|w|_\text{freeze}=(748+611\bar{3})\ \text{J}=\boxed{6.86\times10^{3}\ \text{J}=6.86\ \text{kJ}}$$

At the rate of 100 W = 100 J s^{-1}, the refrigerator would freeze the water in

$$t=\frac{6.86\times10^{3}\ \text{J}}{100\ \text{J s}^{-1}}=\boxed{68.6\ \text{s}}$$

4 Physical transformations of pure substances

Answers to discussion questions

D4.2 Mathematically, we can trace the change in chemical potential when pressure is changed to the pV term within the Gibbs energy (part of the definition of enthalpy); the product changes when the pressure changes. Physically, an incompressible system does not store energy like a spring (or like a highly compressible gas); however, it can transmit energy, as it does in a hydraulic cylinder. Furthermore, an incompressible system under pressure is under stress at a molecular level. Its bonds or intermolecular repulsive forces resist external forces without contraction. Finally, one can observe changes in phases in equilibrium with incompressible liquids (the pressure of their vapours, for example) when pressure is applied to the liquid; see Section 4.4(c).

D4.4

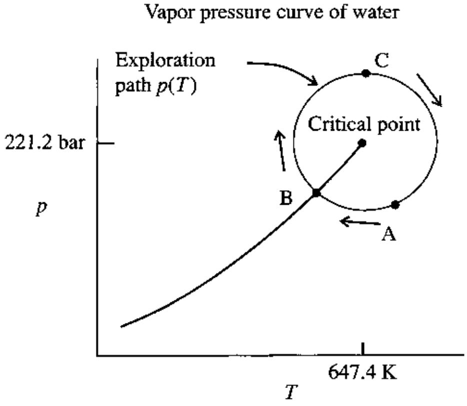


Figure 4.1

Refer to Figure 4.1 above and Figure 4.8 in the text. Starting at point A and continuing clockwise on path $p(T)$ toward point B, we see a gaseous phase only within the container with water at pressures and temperatures $p(T)$. On reaching point B on the vapour-pressure curve, liquid appears on the bottom of the container and a phase boundary or meniscus is evident between the liquid and less dense gas above it. The liquid and gaseous phases are at equilibrium at this point. Proceeding clockwise away from the vapour-pressure curve the meniscus disappears and the system becomes wholly liquid. Continuing along $p(T)$ to point C at the critical temperature no abrupt changes are observed in the isotropic fluid. Before point C is reached, it is possible to return to the vapour-pressure curve and a liquid–gas equilibrium by reducing the pressure isothermally. Continuing clockwise from point C along path $p(T)$ back to point A, no phase boundary is observed even though we now consider the water to have returned to the gaseous state. Additionally, if the pressure is isothermally reduced at any point after point C, it is impossible to return to a liquid–gas equilibrium.

When the path $p(T)$ is chosen to be very close to the critical point, the water appears opaque. At near-critical conditions, densities and refractive indices of both the liquid and gas phases are nearly identical. Furthermore, molecular fluctuations cause spatial variations of densities and refractive indices on a scale large enough to strongly scatter visible light. This is called critical opalescence.

.6 See Section 4.6 for classification of phase transitions. First-order phase transitions show discontinuities in the first derivative of the Gibbs energy with respect to temperature. They are recognized by finite discontinuities in plots of H, U, S, and V against temperature and by an infinite discontinuity in C_p. Second-order phase transitions show discontinuities in the second derivatives of the Gibbs energy with respect to temperature, but the first derivatives are continuous. The second-order transitions are recognized by kinks in plots of H, U, S, and V against temperature, but most easily by a finite discontinuity in a plot of C_p against temperature. A λ-transition shows characteristics of both first- and second-order transitions and, hence, is difficult to classify by the Ehrenfest scheme. It resembles a first-order transition in a plot of C_p against T, but appears to be a higher-order transition with respect to other properties.

At the molecular level first-order transitions are associated with discontinuous changes in the interaction energies between the atoms or molecules constituting the system and in the volume they occupy. One kind of second-order transition may involve only a continuous change in the arrangement of the atoms from one crystal structure (symmetry) to another while preserving their orderly arrangement. In one kind of λ-transition, called an order–disorder transition, randomness is introduced into the atomic arrangement. See Figures 4.19 to 4.22 of the text.

Solutions to exercises

4.1(b) The phase rule (eqn 4.1) relates the number of phases (P), components (C), and degrees of freedom (F) of a thermodynamic system:

$$F = C - P + 2$$

Restricting to pure substances ($C = 1$) and rearranging for phases gives

$$P = 3 - F$$

Areas in the phase diagram have two degrees of freedom; one can vary pressure and temperature independently (within limits) and stay within the area. Thus, $F = 2$ and $P = 1$ in areas. Lines have one degree of freedom; one can vary pressure or temperature, but to stay on the line the value of the other is determined by the line. Thus, $F = 1$ and $P = 2$ on lines. Points on the phase diagram have zero degrees of freedom; one can vary neither pressure nor temperature on a given point. Thus, $F = 0$ and $P = 3$ on points.

(a) is in an area, so there is a $\boxed{\text{single phase}}$. (b) and (c) are points, so there are $\boxed{\text{three phases}}$ present.

(d) is on a line, so there are $\boxed{\text{two phases}}$ present.

E4.2(b) For pure substances (one-component systems), the chemical potential is the molar Gibbs energy:

$$dG = (\mu_2 - \mu_1)dn$$

so $\Delta G = (\mu_2 - \mu_1)n = (-8.3\ \text{kJ mol}^{-1})(0.15 \times 10^{-3}\ \text{mol}) = +1.2 \times 10^{-3}\ \text{kJ} = \boxed{1.2\ \text{J}}$

E4.3(b) The difference between the definition of normal and standard transition temperatures is the pressure at which the transition takes place: normal refers to exactly 1 atm (101325 Pa), while standard refers to exactly 1 bar (10^5 Pa). At the standard boiling temperature and pressure, the liquid and gas phases are in equilibrium, so their chemical potentials are equal:

$$\mu_{\text{liquid}}(T_{\text{std}}, p_{\text{std}}) = \mu_{\text{gas}}(T_{\text{std}}, p_{\text{std}})$$

The same can be said at the normal boiling temperature and pressure:

$$\mu_{\text{liquid}}(T_{\text{norm}}, p_{\text{norm}}) = \mu_{\text{gas}}(T_{\text{norm}}, p_{\text{norm}})$$

Eqns 4.2 and 4.3 show how the chemical potential changes with temperature and pressure, so for small changes we can write

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dp = -S_m dT + V_m dp$$

Assuming that the differences between standard and normal boiling point are small enough, we can equate the differences in the chemical potentials of the two phases:

$$\Delta\mu_{\text{gas}} = -S_{\text{m,gas}}\Delta T + V_{\text{m,gas}}\Delta p = -S_{\text{m,liquid}}\Delta T + V_{\text{m,liquid}}\Delta p = \Delta\mu_{\text{liquid}}$$

where Δp is defined as $p_{\text{norm}} - p_{\text{std}}$. Rearrange to isolate ΔT:

$$(S_{\text{m,liquid}} - S_{\text{m,gas}})\Delta T = (V_{\text{m,liquid}} - V_{\text{m,gas}})\Delta p$$

$$(-\Delta_{\text{vap}}S)\Delta T = (V_{\text{m,liquid}} - V_{\text{m,gas}})\Delta p \approx -V_{\text{m,gas}}\Delta p$$

Use the ideal gas law to find the molar volume of the gas. Also, we need to find $\Delta_{\text{vap}}S$ or to use Trouton's rule (eqn 3.20):

$$\Delta T \approx \frac{V_{\text{m,gas}}\Delta p}{\Delta_{\text{vap}}S} = \frac{RT\Delta p}{p\Delta_{\text{vap}}S} = \frac{RT_b^2\Delta p}{p\Delta_{\text{vap}}H} = \frac{(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1})(373\ \text{K})^2(1325\ \text{Pa})}{(10^5\ \text{Pa})(40.656 \times 10^3\ \text{J})}$$

$$= \boxed{0.38\ \text{K}}$$

That is, the normal boiling temperature is 0.38 K higher than the standard boiling temperature.

E4.4(b) Use the phase rule (eqn 4.1)

$$F = C - P + 2$$

to solve for the number of phases:

$$P = C - F + 2 = 4 - F + 2 = 6 - F \le \boxed{6}$$

The maximum number of phases in equilibrium occurs when the number of degrees of freedom is at a minimum, namely zero; that number is six.

.5(b) Eqn 4.2 shows how the chemical potential changes with temperature

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_p dT = -S_m dT$$

so $\Delta\mu = -\int S_m dT = -S_m \Delta T = -53\ \text{J K}^{-1}\,\text{mol}^{-1} \times (1000 - 100)\ \text{K}$

$$= \boxed{4.8 \times 10^4\ \text{J mol}^{-1}} = \boxed{48\ \text{kJ mol}^{-1}}$$

Note: As the problem stated, we assumed that the entropy is constant over the temperature range.

4.6(b) Eqn 4.3 shows how the chemical potential changes with pressure

$$d\mu = \left(\frac{\partial \mu}{\partial p}\right)_T dp = V_m dp = \frac{M}{\rho} dp$$

so $\Delta\mu = \int \frac{M}{\rho} dp = \frac{M}{\rho}\Delta p = \frac{78.11\ \text{g mol}^{-1}}{0.879\ \text{g cm}^{-3}} \times (10 \times 10^6 - 100 \times 10^3)\ \text{Pa} \times \frac{1\ \text{m}^3}{10^6\ \text{cm}^3}$

$$= \boxed{8.8 \times 10^2\ \text{J mol}^{-1}} = \boxed{0.088\ \text{kJ mol}^{-1}}$$

Note: We assumed that the sample is incompressible.

E4.7(b) The effect on vapour pressure of a change in applied external pressure on a liquid is given by eqn 4.4:

$$p = p^* e^{V_m(l)\Delta P/RT}$$

For liquid naphthalene, the molar volume is

$$V_m = \frac{M}{\rho} = \frac{118.16\ \text{g mol}^{-1}}{0.962\ \text{g cm}^{-3}} = 122.8\ \text{cm}^3\,\text{mol}^{-1}$$

so $\frac{V_m(l)\Delta P}{RT} = \frac{122.8\ \text{cm}^3\,\text{mol}^{-1} \times (15 \times 10^6 - 1.0 \times 10^5)\ \text{Pa}}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1} \times 368\ \text{K}} \times \frac{1\ \text{m}^3}{10^6\ \text{cm}^3} = 0.598$

and $p = p^* e^{V_m(l)\Delta P/RT} = (2.0\ \text{kPa})e^{0.598} = \boxed{3.6\ \text{kPa}}$

E4.8(b) Use the Clapeyron equation (eqn 4.6)

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$$

Assume that $\Delta_{fus}S$ and $\Delta_{fus}T$ are independent of temperature:

$$\Delta_{fus}S = \Delta_{fus}V \times \left(\frac{dp}{dT}\right) \approx \Delta_{fus}V \times \frac{\Delta p}{\Delta T}$$

$$\Delta_{fus}S = (152.6\ \text{cm}^3\,\text{mol}^{-1} - 142.0\ \text{cm}^3\,\text{mol}^{-1}) \times \frac{(1.2 \times 10^6\ \text{Pa} - 1.01 \times 10^5\ \text{Pa})}{429.26\ \text{K} - 427.15\ \text{K}}$$

$$= (10.6\ \text{cm}^3\,\text{mol}^{-1}) \times \left(\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}\right) \times (5.21 \times 10^5\ \text{Pa K}^{-1})$$

$$= 5.52\ \text{Pa m}^3\,\text{K}^{-1}\,\text{mol}^{-1} = \boxed{+5.5\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

At the melting temperature

$$\Delta_{\text{fus}}H = T_f\Delta_{\text{fus}}S = (427.15\text{ K}) \times (5.5\bar{2}\text{ J K}^{-1}\text{ mol}^{-1}) = \boxed{+2.4\text{ kJ mol}^{-1}}$$

E4.9(b) Assume that the vapour is a perfect gas and $\Delta_{\text{vap}}H$ is independent of temperature

$$p = p^*\,\mathrm{e}^{-\chi}, \quad \chi = \left(\frac{\Delta_{\text{vap}}H}{R}\right) \times \left(\frac{1}{T} - \frac{1}{T^*}\right) [4.12], \quad \ln\frac{p^*}{p} = \chi$$

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H}\ln\frac{p^*}{p}$$

$$= \frac{1}{293.2\text{ K}} + \frac{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}{32.7 \times 10^3\text{ J mol}^{-1}} \times \ln\left(\frac{58.0}{66.0}\right) = 3.37\bar{8} \times 10^{-3}\text{ K}^{-1}$$

$$\text{Hence, } T = \frac{1}{3.37\bar{8} \times 10^{-3}\text{ K}^{-1}} = 296\text{ K} = \boxed{23°\text{C}}$$

E4.10(b) Integrating the Clausius–Clapeyron eqation (4.11) yields an expression for $\ln p$:

$$\int \mathrm{d}\ln p = \int \frac{\Delta_{\text{vap}}H}{RT^2}\mathrm{d}T$$

$$\text{so} \quad \ln p = \text{constant} - \frac{\Delta_{\text{vap}}H}{RT}$$

Therefore, $\Delta_{\text{vap}}H = 3036.8\text{ K} \times R = 8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times (3036.8\text{ K}) = \boxed{+25.25\text{ kJ mol}^{-1}}$

E4.11(b) (a) The indefinitely integrated form of eqn 4.11 is used as in Exercise 4.10(a).

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}}H}{RT} \quad \text{or} \quad \log p = \text{constant} - \frac{\Delta_{\text{vap}}H}{2.303\,RT}$$

Thus, $\Delta_{\text{vap}}H = 1625\text{ K} \times R \times 2.303 = 1625\text{ K} \times 8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times 2.303$

$$= \boxed{31.11\text{ kJ mol}^{-1}}$$

(b) The normal boiling point corresponds to $p = 1.000\text{ atm} = 760\text{ Torr}$,

$$\text{so} \quad \log 760 = 8.750 - \frac{1625\text{ K}}{T}$$

$$\text{and} \quad T = \frac{1625\text{ K}}{8.750 - \log 760} = \boxed{276.9\text{ K}}$$

E4.12(b)

$$\Delta T \approx \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}S} \times \Delta p\,[4.6 \text{ and Exercise 4.8(a)}]$$

$$\approx \frac{T_f\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p = \frac{T_f M\Delta p}{\Delta_{\text{fus}}H} \times \Delta\left(\frac{1}{\rho}\right) [V_m = M/\rho]$$

Normal freezing point is $T_f = (273.15 - 3.65)\ \text{K} = 269.50\ \text{K}$ at a pressure of 1 atm, which is about 0.1 MPa. Thus, to the nearest MPa, $\Delta p = 100\ \text{MPa} = 1.00 \times 10^8\ \text{Pa}$

$$\Delta T \approx \frac{269.50\ \text{K} \times 46.1\ \text{g mol}^{-1} \times (1.00 \times 10^8\ \text{Pa})}{8.68 \times 10^3\ \text{J mol}^{-1}} \times \left(\frac{1}{0.789\ \text{g cm}^{-3}} - \frac{1}{0.801\ \text{g cm}^{-3}}\right) \approx 2.7\ \text{K}$$

Therefore, at 100 MPa, $T_f = (269.50 + 2.7)\ \text{K} = \boxed{27.2\ \text{K}}$ or $\boxed{-1.0°\text{C}}$.

4.13(b) The rate of loss of mass of water may be expressed as

$$\frac{dm}{dt} = \frac{d}{dt}(nM), \quad \text{where} \quad n = \frac{q}{\Delta_{\text{vap}}H}$$

Thus, $\dfrac{dn}{dt} = \dfrac{dq/dt}{\Delta_{\text{vap}}H} = \dfrac{(0.87 \times 10^3\ \text{W m}^{-2}) \times (10^4\ \text{m}^2)}{44.0 \times 10^3\ \text{J mol}^{-1}} = 20\bar{0}\ \text{mol s}^{-1}$

and $\dfrac{dm}{dt} = (200\ \text{mol s}^{-1}) \times (18.02\ \text{g mol}^{-1}) = \boxed{3.6\ \text{kg s}^{-1}}$

4.14(b) The equilibrium vapour pressure of ice at −5°C is 0.40 kPa. Therefore, the frost would sublime. A partial pressure of 0.40 kPa or more would ensure that the frost remains.

4.15(b) (a) According to Trouton's rule (Section 3.3(b))

$$\Delta_{\text{vap}}H \approx 85\ \text{J K}^{-1}\text{mol}^{-1} \times T_b = 85\ \text{J K}^{-1}\text{mol}^{-1} \times 342.2\ \text{K} = \boxed{29.1\ \text{kJ mol}^{-1}}$$

(b) Use the integrated form of the Clausius–Clapeyron equation (eqn 4.12) rearranged to

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At $T_1 = 342.2\ \text{K}$, $p_1 = 1.000\ \text{atm}$ [normal boiling point]; thus, at 25°C

$$\ln\left(\frac{p_2}{1.000\ \text{atm}}\right) = \left(\frac{2.91 \times 10^4\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\right) \times \left(\frac{1}{342.2\ \text{K}} - \frac{1}{298.2\ \text{K}}\right) = -1.51$$

and $p_2 = e^{-1.51}\ \text{atm} = \boxed{0.22\ \text{atm}}$

At 60°C, $\ln\left(\dfrac{p_2}{1.000\ \text{atm}}\right) = \left(\dfrac{2.91 \times 10^4\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\right) \times \left(\dfrac{1}{342.2\ \text{K}} - \dfrac{1}{333.2\ \text{K}}\right) = -0.276$

and $p_2 = e^{-0.276}\ \text{atm} = \boxed{0.76\ \text{atm}}$

4.16(b) $\Delta T = T_f(10\ \text{MPa}) - T_f(0.1\ \text{MPa}) = \dfrac{T_f \Delta p M}{\Delta_{\text{fus}}H} \Delta\left(\dfrac{1}{\rho}\right)$ [Exercise 4.12(b)]

$$\Delta T = \left(\frac{(273.15\ \text{K}) \times 9.9 \times 10^6\ \text{Pa} \times 18.0\ \text{g mol}^{-1}}{6.01 \times 10^3\ \text{J mol}^{-1}}\right) \times \left(\frac{1}{0.998\ \text{g cm}^{-3}} - \frac{1}{0.915\ \text{g cm}^{-3}}\right) = -0.74\ \text{K}$$

$$T_f(10\ \text{MPa}) = (273.15 - 0.74)\ \text{K} = \boxed{272.41\ \text{K}}$$

E4.17(b) $\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV) = 43.5\ \text{kJ mol}^{-1}$

$$\Delta_{\text{vap}}(pV) = p\Delta_{\text{vap}}V = p(V_{\text{gas}} - V_{\text{liq}}) \approx pV_{\text{gas}} = RT\ [\text{perfect gas}]$$

$$\Delta_{\text{vap}}(pV) \approx (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (352\ \text{K}) = 2.93 \times 10^3\ \text{J mol}^{-1}$$

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H} = \frac{2.93\ \text{kJ mol}^{-1}}{43.5\ \text{kJ mol}^{-1}} = \boxed{0.0673} = 6.73\%$$

Solutions to problems

Solutions to numerical problems

P4.2 Use the definite integral form of the Clausius–Clapeyron equation [Exercise 4.15(b)].

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At $T_1 = (273.15 - 29.2)\ \text{K} = 244.0\ \text{K}$ (normal boiling point), $p_1 = 1.000\ \text{atm}$, thus, at 40°C

$$\ln\left(\frac{p_2}{1.000\ \text{atm}}\right) = \left(\frac{20.25 \times 10^3\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\right) \times \left(\frac{1}{244.0\ \text{K}} - \frac{1}{313.2\ \text{K}}\right) = 2.205$$

and $p_2 = 1.000\ \text{atm} \times e^{2.205} = \boxed{9.07\ \text{atm}}$

COMMENT. Three significant figures are not really warranted in this answer because of the approximations employed.

P4.4 (a) $\left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{s})}{\partial T}\right)_p = -S_{\text{m}}(\text{l}) + S_{\text{m}}(\text{s}) = -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_{\text{f}}}$ [4.13]

$$= \frac{-6.01 \times 10^3\ \text{J mol}^{-1}}{273.15\ \text{K}} = \boxed{-22.0\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

(b) $\left(\frac{\partial\mu(\text{g})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p = -S_{\text{m}}(\text{g}) + S_{\text{m}}(\text{l}) = -\Delta_{\text{vap}}S = \frac{-\Delta_{\text{vap}}H}{T_{\text{b}}}$

$$= \frac{-40.6 \times 10^3\ \text{J mol}^{-1}}{373.15\ \text{K}} = \boxed{-108.8\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

(c) $\mu(\text{l},-5°\text{C}) - \mu(\text{s},-5°\text{C}) = \mu(\text{l},-5°\text{C}) - \mu(\text{l},0°\text{C}) - \{\mu(\text{s},-5°\text{C}) - \mu(\text{s},0°\text{C})\}$

because $\mu(\text{l},0°\text{C}) = \mu(\text{s},0°\text{C})$

Thus, $\mu(\text{l},-5°\text{C}) - \mu(\text{s},-5°\text{C}) = \Delta\mu(\text{l}) - \Delta\mu(\text{s})$

where $\Delta\mu$ is the difference in chemical potential of a given phase at −5°C compared to that at normal freezing temperature.

$$\Delta\mu \approx \left(\frac{\partial\mu}{\partial T}\right)_p \Delta T = -S_{\text{m}}\Delta T\ [4.2],$$

so $\{\mu(\text{l},-5°\text{C})-\mu(\text{l},0°\text{C})\}-\{\mu(\text{s},-5°\text{C})-\mu(\text{s},0°\text{C})\}=-\Delta_{\text{fus}}S\Delta T$

$$\mu(\text{l},-5°\text{C})-\mu(\text{s},-5°\text{C})=-(+22.0\ \text{J K}^{-1}\,\text{mol}^{-1})\times(-5\ \text{K})=\boxed{+11\bar{0}\ \text{J mol}^{-1}}$$

Since $\mu(\text{l},-5°\text{C})>\mu(\text{s},-5°\text{C})$, there is a thermodynamic tendency to freeze.

4.6 $$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V}\,[4.6]=\frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}\,[4.7]$$

Thus, $\mathrm{d}T=\dfrac{T\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H}\mathrm{d}p$

Integrate both sides:

$$\Delta T=\int_{T_{\text{f,top}}}^{T_{\text{f,bot}}}\mathrm{d}T=\int_{p_{\text{top}}}^{p_{\text{bot}}}\frac{T_{\text{m}}\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H}\mathrm{d}p=\frac{T_{\text{m}}\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H}\Delta p\ \text{[assuming the integrand is constant]}$$

Now, $\Delta p=p_{\text{bot}}-p_{\text{top}}=\rho gh$

$$\text{so}\quad \Delta T=\frac{T_{\text{m}}\rho gh\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H}$$

$$=\frac{(234.3\ \text{K})\times(13.6\ \text{g cm}^{-3})\times(9.81\ \text{m s}^{-2})\times(10.0\ \text{m})\times(0.517\ \text{cm}^3\,\text{mol}^{-1})}{2.292\times10^3\ \text{J mol}^{-1}}\times\frac{1\ \text{kg}}{10^3\ \text{g}}$$

$$=0.071\ \text{K}$$

Therefore, the freezing point changes to $\boxed{234.4\ \text{K}}$.

4.8 Integrating the Clausius–Clapeyron eqation (4.11) yields an expression for $\ln p$:

$$\ln p=\text{constant}-\frac{\Delta_{\text{vap}}H}{RT}$$

Therefore, plot $\ln p$ against $1/T$ and identify $-\Delta_{\text{vap}}H/R$ as the slope of the plot. Construct the following table:

$\theta/°\text{C}$	0	20	40	50	70	80	90	100
T/K	273	293	313	323	343	353	363	373
$1000\ \text{K}/T$	3.66	3.41	3.19	3.10	2.92	2.83	2.75	2.68
$\ln(p/\text{kPa})$	0.652	1.85	2.87	3.32	4.13	4.49	4.83	5.14

The points are plotted in Figure 4.2. The slope is –4569 K, so

$$\frac{-\Delta_{\text{vap}}H}{R}=-4569\ \text{K}\quad\text{or}\quad\Delta_{\text{vap}}H=\boxed{+38.0\ \text{kJ mol}^{-1}}$$

The normal boiling point occurs at $p=1\ \text{atm}=101.3\ \text{kPa}$, or at $\ln(p/\text{kPa})=4.618$, which from the figure corresponds to $1000\ \text{K}/T=2.80$. Therefore, $T_{\text{b}}=\boxed{357\ \text{K}\ (84°\text{C}).}$ The accepted value is 83°C.

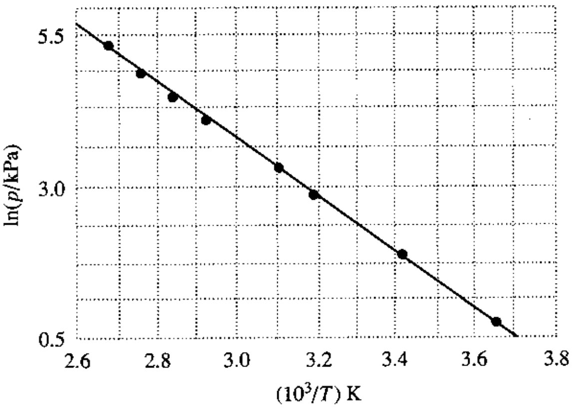


Figure 4.2

P4.10 The equations describing the coexistence curves for the three states are

(a) Solid–liquid boundary

$$p = p^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V}\ln\frac{T}{T^*}\ [4.8]$$

(b) Liquid–vapour boundary

$$p = p^*\,\mathrm{e}^{-\chi}, \quad \chi = \frac{\Delta_{\text{vap}}H}{R}\times\left(\frac{1}{T}-\frac{1}{T^*}\right)[4.12]$$

(c) Solid–vapour boundary

$$p = p^*\,\mathrm{e}^{-\chi}, \quad \chi = \frac{\Delta_{\text{sub}}H}{R}\times\left(\frac{1}{T}-\frac{1}{T^*}\right)\ \text{[analogous to 4.12]}$$

We need $\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H = 41.4\ \text{kJ mol}^{-1}$

$$\Delta_{\text{fus}}V = M\times\left(\frac{1}{\rho(\text{l})}-\frac{1}{\rho(\text{s})}\right) = \left(\frac{78.11\ \text{g mol}^{-1}}{\text{g cm}^{-3}}\right)\times\left(\frac{1}{0.879}-\frac{1}{0.891}\right) = +1.20\ \text{cm}^3\,\text{mol}^{-1}$$

After insertion of these numerical values into the above equations, we obtain

$$\text{(a)}\quad p = p^* + \left(\frac{10.6\times10^{3}\ \text{J mol}^{-1}}{1.20\times10^{-6}\,\text{m}^3\,\text{mol}^{-1}}\right)\ln\frac{T}{T^*}$$

$$= p^* + 8.86\times10^{9}\ \text{Pa}\times\ln\frac{T}{T^*} = p^* + (6.64\times10^{7}\ \text{Torr})\ln\frac{T}{T^*}\ [1\ \text{Torr} = 133.3\ \text{Pa}]$$

This line is plotted as *a* in Figure 4.3, starting at the triple point $(p^*, T^*) = (36\ \text{Torr}, 5.50°\text{C}\ (278.65\ \text{K}))$.

$$\text{(b)}\quad \chi = \left(\frac{30.8\times10^{3}\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}}\right)\times\left(\frac{1}{T}-\frac{1}{T^*}\right) = (370\bar{4}\ \text{K})\times\left(\frac{1}{T}-\frac{1}{T^*}\right)$$

$$p = p^*\,\mathrm{e}^{-370\bar{4}\,\text{K}\times(1/T-1/T^*)}$$

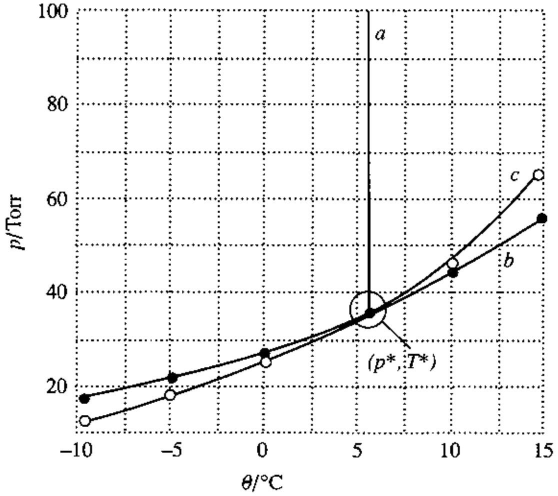


Figure 4.3

This equation is plotted as curve b in Figure 4.3, starting from the triple point (p^*,T^*).

(c) $$\chi = \left(\frac{41.4\times10^{3}\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\right)\times\left(\frac{1}{T}-\frac{1}{T^*}\right) = (497\bar{9}\ \mathrm{K})\times\left(\frac{1}{T}-\frac{1}{T^*}\right)$$

$$p = p^*\,\mathrm{e}^{-497\bar{9}\,\mathrm{K}\times(1/T-1/T^*)}$$

These points are plotted as curve c in Figure 4.3, starting from the triple point (p^*,T^*). The lighter lines in Figure 4.3 represent extensions of lines b and c into regions where the liquid and solid states, respectively, are not stable.

4.12 The slope of the solid–vapour coexistence curve is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sub}}H}{T\Delta_{\mathrm{sub}}V}\ \text{[analogous to 4.10] so } \Delta_{\mathrm{sub}}H = T\Delta_{\mathrm{sub}}V\frac{\mathrm{d}p}{\mathrm{d}T}$$

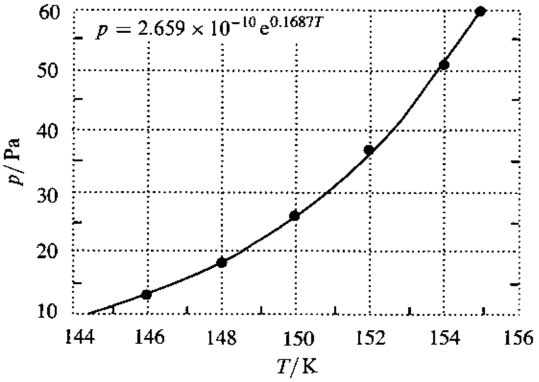


Figure 4.4

The slope can be obtained by differentiating an equation fit to the coexistence curve (Figure 4.4). Fit the data to an exponential function or take natural logarithms of the pressures and make a linear fit to the transformed data. The fit equation is

$$p/\mathrm{Pa} = 2.659\times10^{-10}\,\mathrm{e}^{0.1687T/\mathrm{K}}$$

so $\dfrac{dp}{dT} = (2.659 \times 10^{-10}\ \mathrm{Pa}) \times (0.1687\ \mathrm{K}^{-1}) \times e^{0.1687T/\mathrm{K}} = 4.41\ \mathrm{Pa\ K^{-1}}$ at 150 K

The change in volume is essentially the volume of the vapour

$$V_m = \frac{RT}{p} = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (150\ \mathrm{K})}{(2.659 \times 10^{-10}\ \mathrm{Pa}) \times e^{0.1687\times150}} = 47.7\ \mathrm{m}^3$$

So, $\Delta_{\mathrm{sub}}H^{\ominus} = (150\ \mathrm{K}) \times (47.7\ \mathrm{m}^3) \times 4.41\ \mathrm{Pa\ K^{-1}} = 3.16 \times 10^4\ \mathrm{J\ mol^{-1}}$

$$= \boxed{31.6\ \mathrm{kJ\ mol^{-1}}}$$

Solutions to theoretical problems

P4.14 $dH = C_p dT + V dp$ implies $d\Delta H = \Delta C_p dT + \Delta V dp$

where Δ signifies a difference between phases. Along a phase boundary dp and dT are related by

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}\ [4.7 \text{ or } 4.10]$$

Therefore,

$$d\Delta H = \left(\Delta C_p + \Delta V \times \frac{\Delta H}{T\Delta V}\right)dT = \left(\Delta C_p + \frac{\Delta H}{T}\right)dT \quad \text{and} \quad \frac{d\Delta H}{dT} = \Delta C_p + \frac{\Delta H}{T}$$

Then, since

$$\frac{d}{dT}\left(\frac{\Delta H}{T}\right) = \frac{1}{T}\frac{d\Delta H}{dT} - \frac{\Delta H}{T^2} = \frac{1}{T}\left(\frac{d\Delta H}{dT} - \frac{\Delta H}{T}\right)$$

substituting the first result gives

$$\frac{d}{dT}\left(\frac{\Delta H}{T}\right) = \frac{\Delta C_p}{T}$$

Therefore,

$$d\left(\frac{\Delta H}{T}\right) = \frac{\Delta C_p dT}{T} = \boxed{\Delta C_p\, d\ln T}$$

P4.16 Eqn 4.4 gives the vapour pressure of a liquid under an additional applied pressure ΔP:

$$p = p^* e^{V_m(l)\Delta P/RT}$$

The applied pressure is the hydrostatic pressure of the liquid overlying the depth d:

$$\Delta P = \rho g d$$

The molar volume of the liquid is

$$V_m(l) = M/\rho$$

Substituting into eqn 4.4 yields

$$\boxed{p = p^* \, \mathrm{e}^{Mgd/RT}}$$

For a 10-m column of water at 25°C,

$$\frac{Mgd}{RT} = \frac{(18.02 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (9.81\,\mathrm{m\,s^{-2}}) \times (10\,\mathrm{m})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})} = 7.1 \times 10^{-4}$$

$$\text{so} \quad \frac{p}{p^*} = \mathrm{e}^{7.1 \times 10^{-4}} \approx 1 + 7.1 \times 10^{-4}$$

That is, the fractional increase in vapour pressure is $\boxed{7.1 \times 10^{-4}}$ or $\boxed{0.071\%}$.

4.18 In each phase the slopes of curves of chemical potential plotted against temperature are

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_\mathrm{m} \; [4.2]$$

The curvatures of the graphs are given by

$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_p = -\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_p$$

To evaluate this derivative, consider dS at constant p:

$$\mathrm{d}S = \frac{\mathrm{d}q_\mathrm{rev}}{T} = \frac{\mathrm{d}H}{T} = \frac{C_p \mathrm{d}T}{T} \quad \text{so} \quad \left(\frac{\partial^2 \mu}{\partial T^2}\right)_p = -\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_p = -\frac{C_{p,\mathrm{m}}}{T}$$

Since $C_{p,\mathrm{m}}$ is necessarily positive, the curvatures in all states of matter are necessarily negative. $C_{p,\mathrm{m}}$ is often largest for the liquid state, although not always. In any event, it is the ratio $C_{p,\mathrm{m}}/T$ that determines the magnitude of the curvature, so no general answer can be given for the state with the greatest curvature. It depends on the substance.

4.20 $S = S(T,p)$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \; \text{[Problem 4.18]}; \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \; \text{[Table 3.5]} = -\alpha V_\mathrm{m}$$

$$\mathrm{d}q_\mathrm{rev} = T\,\mathrm{d}S = C_p \mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p$$

$$C_S = \left(\frac{\partial q}{\partial T}\right)_S = C_p - TV\alpha\left(\frac{\partial p}{\partial T}\right)_S = \boxed{C_p - \alpha V \times \frac{\Delta_\mathrm{trs} H}{\Delta_\mathrm{trs} V}} \; [4.7]$$

Solutions to applications

P4.22 (a) The Dieterici equation of state is purported to have good accuracy near the critical point. It does fail badly at high densities where V_m begins to approach the value of the Dieterici coefficient b. We will use it to derive a practical equation for the computations.

$$p_r = \frac{e^2 T_r e^{-2/T_r V_r}}{2V_r - 1} \text{ [Table 1.7]}$$

Substitution of the derivative

$$\left(\frac{\partial p_r}{\partial T_r}\right)_{V_r} = \frac{(2 + T_r V_r) p_r}{T_r^2 V_r}$$

into the reduced form of eqn 3.51 gives

$$\left(\frac{\partial U_r}{\partial V_r}\right)_{T_r} = T_r \left(\frac{\partial p_r}{\partial T_r}\right)_{V_r} - p_r = \frac{2p_r}{T_r V_r} \quad \left[U_r = \frac{U}{p_c V_c}\right]$$

Integration along the isotherm T_r from an infinite volume to V_r yields the practical computational equation.

$$\boxed{\Delta U_r(T_r, V_r) = -\int_{T_r\text{constant}}^{\infty} \frac{2p_r(T_r, V_r)}{T_r V_r} \mathrm{d}V_r}$$

The integration is performed with mathematical software.

(b) See Figure 4.5(a).

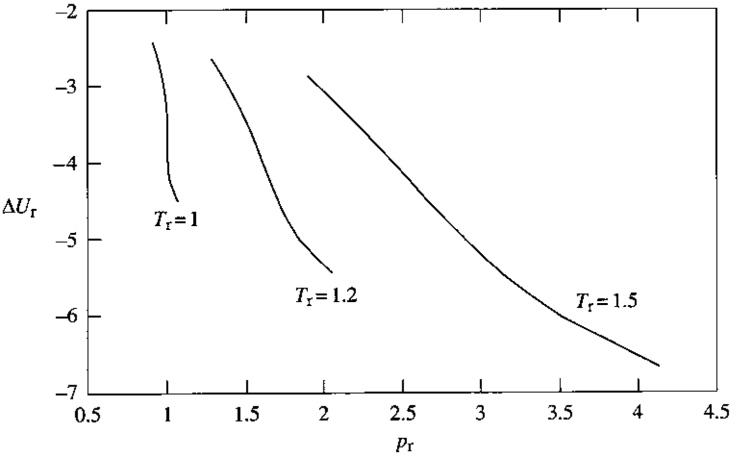


Figure 4.5(a)

(c) $\delta(T_r, V_r) = (-p_c \Delta U_r / V_r)^{1/2}$, where $p_c = 72.9$ atm

Carbon dioxide should have solvent properties similar to liquid carbon tetrachloride ($8 \le \delta \le 9$) when the reduced pressure is in the approximate range $\boxed{0.85 \text{ to } 0.90 \text{ when } T_r = 1}$. See Figure 4.5(b).

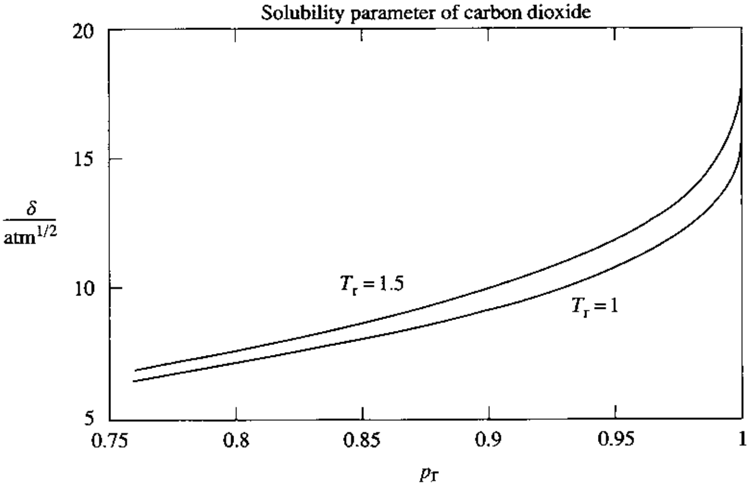


Figure 4.5(b)

4.24 C(graphite) $\rightleftharpoons$ C(diamond) $\Delta_rG = 2.8678\ \mathrm{kJ\ mol^{-1}}$ at $T = 25°\mathrm{C}$

We want the pressure at which $\Delta_rG = 0$; above that pressure the reaction will be spontaneous. Eqn 3.53 determines the rate of change of Δ_rG with p at constant T.

$$(1)\quad \left(\frac{\partial\Delta_rG}{\partial p}\right)_T = \Delta_rV = (V_D - V_G)M$$

where M is the molar mass of carbon; V_D and V_G are the specific volumes of diamond and graphite, respectively. $\Delta_rG(p)$ may be expanded in a Taylor series around the pressure $p_0 = 100$ kPa.

$$(2)\quad \Delta_rG(p) = \Delta_rG(p_0) + \left(\frac{\partial\Delta_rG(p_0)}{\partial p}\right)_T (p - p_0) + \frac{1}{2}\left(\frac{\partial^2\Delta_rG(p_0)}{\partial p^2}\right)_T (p - p_0)^2 + \cdots$$

We will neglect the third and higher-order terms in $(p - p_0)$; the derivative of the first-order term can be calculated from eqn (1). An expression for the derivative of the second-order term can be derived from eqn (1).

$$(3)\quad \left(\frac{\partial^2\Delta_rG}{\partial p^2}\right)_T = \left\{\left(\frac{\partial V_D}{\partial p}\right)_T - \left(\frac{\partial V_G}{\partial p}\right)_T\right\}M = (V_G\kappa_{T,G} - V_D\kappa_{T,D})M \ [2.43]$$

Calculating the derivatives of eqns (1) and (2) at p_0,

$$(4)\quad \left(\frac{\partial\Delta_rG(p_0)}{\partial p}\right)_T = (0.284 - 0.444)\times\left(\frac{\mathrm{cm^3}}{\mathrm{g}}\right)\times\left(\frac{12.01\ \mathrm{g}}{\mathrm{mol}}\right) = -1.92\ \mathrm{cm^3\ mol^{-1}}$$

$$(5)\quad \left(\frac{\partial^2\Delta_rG(p_0)}{\partial p^2}\right)_T = \{0.444(3.04\times10^{-8}) - 0.284(0.187\times10^{-8})\}$$

$$\times\left(\frac{\mathrm{cm^3\ kPa^{-1}}}{\mathrm{g}}\right)\times\left(\frac{12.01\ \mathrm{g}}{\mathrm{mol}}\right)$$

$$= 1.56\times10^{-7}\ \mathrm{cm^3\ kPa^{-1}\ mol^{-1}}$$

It is convenient to convert the value of $\Delta_r G(p_0)$ to the units $\text{cm}^3\ \text{kPa mol}^{-1}$

$$(6)\quad \Delta_r G(p_0) = 2.8678 \times 10^3\ \text{J mol}^{-1} \times \left(\frac{10^6\ \text{cm}^3}{\text{m}^3}\right) \times \left(\frac{1\ \text{kPa}}{10^3\ \text{Pa}}\right)$$

$$= 2.8678 \times 10^6\ \text{cm}^3\ \text{kPa mol}^{-1}$$

Setting $\chi = p - p_0$, and dividing through by $\text{cm}^3\ \text{mol}^{-1}$, eqns (2) and (3)–(6) give

$$2.8678 \times 10^6\ \text{kPa} - 1.92\chi + (7.80 \times 10^{-8}\ \text{kPa}^{-1})\chi^2 = 0$$

when $\Delta_r G(p) = 0$. One real root of this equation is

$$\chi = 1.60 \times 10^6\ \text{kPa} = p - p_0$$

or $\quad p = 1.60 \times 10^6\ \text{kPa} - 100\ \text{kPa} = 1.60 \times 10^6\ \text{kPa} = \boxed{1.60 \times 10^4\ \text{bar}}$.

Above this pressure the reaction is spontaneous. The other real root is much higher, 2.3×10^7 kPa.

Question. What interpretation might you give to the other real root?

5

Simple mixtures

Answers to discussion questions

5.2 For a component in an ideal solution, Raoult's law is $p = xp^*$. For real solutions, the activity, a, replaces the mole fraction, x, and Raoult's law changes to $p = ap^*$.

5.4 A regular solution has an excess entropy of zero, but an excess enthalpy that is non-zero and dependent on composition, perhaps in the manner of eqn 5.28. We can think of a regular solution as one in which the different molecules of the solution are distributed randomly, as in an ideal solution, but have different energies of interaction with each other.

5.6 A theoretical plate in fractional distillation is one evaporation and condensation 'step'. Imagine collecting the first material to vaporize from a mixture and condensing it separate from the original mixture. On a standard temperature–composition phase diagram, such as those shown in Figure 5.37 of the main text, one fractional plate changes the liquid composition from one point to another on the curve that represents the boiling temperature of the liquid by moving horizontally (constant temperature) to the vapour-composition curve and then vertically (constant composition) back to the boiling temperature curve. (In the diagrams of Figure 5.37, the boiling temperature of the liquid is on the left, the vapour composition is on the right; the two curves bound the liquid–vapour coexistence region.) The number of theoretical plates required to achieve a given composition depends on that desired composition, the initial composition of the mixture, and the shape of the liquid–vapour coexistence region.

Solutions to exercises

5.1(b) Total volume $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$, where $n = n_A + n_B$

Total mass $m = n_A M_A + n_B M_B = n\{x_A M_A + (1 - x_A)M_B\}$

$$\text{So,}\quad n = \frac{m}{x_A M_A + (1 - x_A)M_B}$$

$$= \frac{1.000 \times 10^3\,\text{g}}{(0.3713) \times (241.1\,\text{g mol}^{-1}) + (1 - 0.3713) \times (198.2\,\text{g mol}^{-1})}$$

$$= 4.670\,\text{mol}$$

$$\begin{aligned} V &= n(x_A V_A + x_B V_B) \\ &= (4.670\text{ mol}) \times \{(0.3713) \times (188.2) + (1 - 0.3713) \times (176.14)\}\text{ cm}^3\text{ mol}^{-1} \\ &= \boxed{843.5\text{ cm}^3} \end{aligned}$$

E5.2(b) Let W denote water and E ethanol. The total volume of the solution is

$$V = n_W V_W + n_E V_E$$

We are given V_E, we need to determine n_W and n_E in order to solve for V_W, for

$$V_W = \frac{V - n_E V_E}{n_W}$$

Take 100 cm^3 of solution as a convenient sample. The mass of this sample is

$$m = \rho V = (0.9687\text{ g cm}^{-3}) \times (100\text{ cm}^3) = 96.87\text{ g}$$

80% of this mass is water and 20% is ethanol, so the moles of each component are

$$n_W = \frac{(0.80) \times (96.87\text{ g})}{18.02\text{ g mol}^{-1}} = 4.3\text{ mol} \quad \text{and} \quad n_E = \frac{(0.20) \times (96.87\text{ g})}{46.07\text{ g mol}^{-1}} = 0.42\text{ mol}.$$

$$V_W = \frac{V - n_E V_E}{n_W} = \frac{100\text{ cm}^3 - (0.42\text{ mol}) \times (52.2\text{ cm}^3\text{ mol}^{-1})}{4.3\text{ mol}} = \boxed{18\text{ cm}^3\text{ mol}^{-1}}$$

E5.3(b) Check whether p_B/x_B is equal to a constant (K_B).

x	0.010	0.015	0.020
$(p/\text{kPa})/x$	8.2×10^3	8.1×10^3	8.3×10^3

Hence, $K_B = p/x = \boxed{8.2 \times 10^3\text{ kPa}}$ (average value).

E5.4(b) In Exercise 5.3(a), the Henry's law constant was determined for concentrations expressed in mole fractions; $K_B = 8.2 \times 10^3$ kPa. Thus, the concentration must be converted from molality to mole fraction

$$m_A = 1000\text{ g, corresponding to } n_A = \frac{1000\text{ g}}{74.1\text{ g mol}^{-1}} = 13.50\text{ mol}$$

$$\text{Therefore, } x_B = \frac{0.25\text{ mol}}{(0.25\text{ mol}) + (13.50\text{ mol})} = 0.018$$

The pressure is

$$p_B = K_B x_B = (0.018) \times (8.2 \times 10^3\text{ kPa}) = \boxed{1.5 \times 10^2\text{ kPa}}.$$

E5.5(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law.

$$x_A(\text{solvent}) = \frac{p_A}{p_A^*} = \frac{49.62}{50.00} = 0.9924$$

Since $M_A(C_3H_8O) = 60.096\ \text{g mol}^{-1}$,

$$n_A = \frac{250\ \text{g}}{60.096\ \text{g mol}^{-1}} = 4.16\ \text{mol}$$

$$x_A = \frac{n_A}{n_A + n_B} \quad \text{so} \quad n_A + n_B = \frac{n_A}{x_A}.$$

Hence, $n_B = n_A\left(\dfrac{1}{x_A} - 1\right) = 4.16\ \text{mol} \times \left(\dfrac{1}{0.9924} - 1\right) = 3.12 \times 10^{-2}\ \text{mol}$

and $M_B = \dfrac{m_B}{n_B} = \dfrac{8.69\ \text{g}}{3.12 \times 10^{-2}\ \text{mol}} = \boxed{273\ \text{g mol}^{-1}}$

5.6(b) Let B denote the compound and A the solvent, naphthalene. $K_f = 6.94\ \text{K kg mol}^{-1}$ [Table 5.2]

$$M_B = \frac{m_B}{n_B}$$

$$n_B = m_A b_B, \quad \text{where} \quad b_B = \frac{\Delta T}{K_f}\ [5.35]$$

Thus, $M_B = \dfrac{m_B K_f}{m_A \Delta T} = \dfrac{(5.00\ \text{g}) \times (6.94\ \text{K kg mol}^{-1})}{(0.250\ \text{kg}) \times (0.780\ \text{K})} = \boxed{178\ \text{g mol}^{-1}}$

5.7(b) From the osmotic pressure compute the concentration, and from the concentration the freezing point. According to the van't Hoff equation [5.38], the osmotic pressure is

$$\Pi = [\text{B}]RT \quad \text{so} \quad [\text{B}] = \frac{\Pi}{RT} = \frac{n_B}{V_{\text{soln}}}$$

The expression for freezing point depression [eqn 5.35] includes the molality b_B rather than the molarity [B]. In dilute solutions, the two concentration measures are readily related:

$$b_B = \frac{n_B}{m_A} \approx \frac{n_B}{V_{\text{soln}}\rho_{\text{soln}}} = \frac{[\text{B}]}{\rho_{\text{soln}}} = \frac{\Pi}{RT\rho_{\text{soln}}}$$

The freezing point depression is

$$\Delta T = K_f b_B \approx \frac{K_f \Pi}{RT\rho_{\text{soln}}}, \quad \text{where} \quad K_f = 1.86\ \text{K mol}^{-1}\ \text{kg [Table 5.2]}$$

The density of a dilute aqueous solution is approximately that of water:

$$\rho \approx 1.0\ \text{g cm}^{-3} = 1.0 \times 10^3\ \text{kg m}^{-3}$$

So $\Delta T \approx \dfrac{(1.86\ \text{K kg mol}^{-1}) \times (99 \times 10^3\ \text{Pa})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (288\ \text{K}) \times (10^3\ \text{kg m}^{-3})} = 0.077\ \text{K}$

Therefore, the solution will freeze at about $\boxed{-0.077^\circ\text{C}}$.

E5.8(b) The Gibbs energy of mixing perfect gases is

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)\,[5.16] = pV(x_A \ln x_A + x_B \ln x_B)\ \text{[ideal gas]}$$

$$\Delta_{\text{mix}}G = (pV)\times(\tfrac{1}{2}\ln\tfrac{1}{2}+\tfrac{1}{2}\ln\tfrac{1}{2}) = -pV\ln 2$$

$$= -(100\times10^3\ \text{Pa})\times(250\ \text{cm}^3)\left(\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}\right)\times\ln 2 = -17.3\ \text{Pa m}^3 = \boxed{-17.3\ \text{J}}$$

$$\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)\,[5.17] = \frac{-\Delta_{\text{mix}}G}{T} = \frac{-17.3\ \text{J}}{273\ \text{K}} = \boxed{-0.635\ \text{J K}^{-1}}$$

E5.9(b) $\Delta_{\text{mix}}G = nRT\sum_J x_J \ln x_J\ [5.16] \quad \Delta_{\text{mix}}S = -nR\sum_J x_J \ln x_J\ [5.17] = \dfrac{-\Delta_{\text{mix}}G}{T}$

$n = 2.00\ \text{mol}$ and $x_{\text{hexane}} = x_{\text{heptane}} = 0.500$

Therefore,

$$\Delta_{\text{mix}}G = (2.00\ \text{mol})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})\times2\times(0.500\ \ln 0.500)$$

$$= -3.43\times10^3\ \text{J} = \boxed{-3.43\ \text{kJ}}$$

and $\Delta_{\text{mix}}S = \dfrac{-\Delta_{\text{mix}}G}{T} = \dfrac{+3.43\times10^3}{298\ \text{K}} = \boxed{+11.5\ \text{J K}^{-1}}$

For an ideal solution, $\Delta_{\text{mix}}H = 0$, just as it is for a mixture of perfect gases [Section 5.4(a)]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = \Delta_{\text{mix}}G + T\left(\frac{-\Delta_{\text{mix}}G}{T}\right) = \boxed{0}$$

E5.10(b) (a) Benzene and ethylbenzene form nearly ideal solutions, so eqn 5.17 applies.

$$\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)\,[5.17]$$

We need to differentiate eqn 5.17 with respect to x_A and look for the value of x_A at which the derivative is zero. Since $x_B = 1 - x_A$, we need to differentiate

$$\Delta_{\text{mix}}S = -nR\{x_A \ln x_A + (1-x_A)\ln(1-x_A)\}$$

This gives $\left(\text{using } \dfrac{\mathrm{d}\ln x}{\mathrm{d}x} = \dfrac{1}{x}\right)$

$$\frac{\mathrm{d}\Delta_{\text{mix}}S}{\mathrm{d}x_A} = -nR\{\ln x_A + 1 - \ln(1-x_A) - 1\} = -nR\ln\frac{x_A}{1-x_A}$$

which is zero when $x_A = \boxed{\tfrac{1}{2}}$. Hence, the maximum entropy of mixing occurs for the preparation of a mixture that contains equal mole fractions of the two components.

(b) Because entropy of mixing is maximized when $n_E = n_B$ (changing to notation specific to benzene (B) and ethylbenzene (E),

$$\frac{m_E}{M_E} = \frac{m_B}{M_B}$$

This makes the mass ratio

$$\frac{m_B}{m_E} = \frac{M_B}{M_E} = \frac{78.11\text{ g mol}^{-1}}{106.17\text{ g mol}^{-1}} = \boxed{0.7357}$$

5.11(b) With concentrations expressed in molalities, Henry's law [5.23] becomes $p_B = b_B K_B$.

Solving for b, the molality, we have $b_B = \frac{p_B}{K_B} = \frac{x_B p_{\text{total}}}{K_B}$,

where $p_{\text{total}} = 1\text{ atm} = 101.3\text{ kPa}$

For N_2, $K_B = 1.56 \times 10^5\text{ kPa kg mol}^{-1}$ [Table 5.1]

$$b_B = \frac{0.78 \times 101.3\text{ kPa}}{1.56 \times 10^5\text{ kPa kg mol}^{-1}} = \boxed{5.1 \times 10^{-4}\text{ mol kg}^{-1}}$$

For O_2, $K_B = 7.92 \times 10^4\text{ kPa kg mol}^{-1}$ [Table 5.1]

$$b_B = \frac{0.21 \times 101.3\text{ kPa}}{7.92 \times 10^4\text{ kPa kg mol}^{-1}} = \boxed{2.7 \times 10^{-4}\text{ mol kg}^{-1}}$$

5.12(b) As in Exercise 5.11(b), we have $b_B = \frac{p_B}{K_B} = \frac{2.0 \times 101.3\text{ kPa}}{3.01 \times 10^3\text{ kPa kg mol}^{-1}} = 0.067\text{ mol kg}^{-1}$.

Hence, the molality of the solution is about 0.067 mol kg^{-1}. Since molalities and molar concentrations (molarities) for dilute aqueous solutions are numerically approximately equal, the molar concentration is about $\boxed{0.067\text{ mol dm}^{-3}}$.

5.13(b) The ideal solubility in terms of mole fraction is given by eqn 5.37:

$$\ln x_{Pb} = \frac{\Delta_{\text{fus}}H}{R} \times \left(\frac{1}{T_f} - \frac{1}{T}\right)$$

$$= \left(\frac{5.2 \times 10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{mol}^{-1}}\right) \times \left(\frac{1}{600\text{ K}} - \frac{1}{553\text{ K}}\right) = -0.089$$

Therefore, $x_{Pb} = e^{-0.089} = 0.92$.

$$x_{Pb} = \frac{n_{Pb}}{n_{Bi} + n_{Pb}}, \text{ implying that } \quad n_{Pb} = \frac{n_{Bi}x_{Pb}}{1 - x_{Pb}} = \frac{m_{Bi}}{M_{Bi}} \times \frac{x_{Pb}}{1 - x_{Pb}}$$

Hence, the amount of lead that dissolves in 1 kg of bismuth is

$$n_{Pb} = \frac{1000\text{ g}}{209\text{ g mol}^{-1}} \times \frac{0.92}{1 - 0.92} = \boxed{52\text{ mol}}$$

or, in mass units, $m_{Pb} = n_{Pb} \times M_{Pb} = 52\text{ mol} \times 207\text{ g mol}^{-1} = 1.1 \times 10^4\text{ g} = \boxed{11\text{ kg}}$.

COMMENT. A mixture of 11 kg of lead and 1 kg of bismuth would normally be regarded as a solution of bismuth in lead, not the other way around. It is unlikely that such a mixture could be regarded as an ideal dilute solution of lead in bismuth. Under such circumstances eqn 5.37 ought to be considered suggestive at best, rather than quantitative.

E5.14(b) The best value of the molar mass is obtained from values of the data extrapolated to zero concentration, since it is under this condition that the van't Hoff equation [5.38] applies.

$$\Pi V = n_B RT\,[5.38], \quad \text{so} \quad \Pi = \frac{mRT}{MV} = \frac{cRT}{M}, \quad \text{where} \quad c = \frac{m}{V}$$

But the osmotic pressure is also equal to the hydrostatic pressure

$$\Pi = \rho g h\,[1.3], \quad \text{so} \quad h = \left(\frac{RT}{\rho g M}\right)c$$

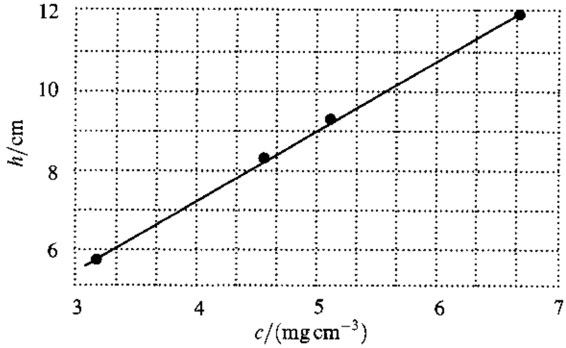


Figure 5.1

Hence, plot h against c and identify the slope as $\frac{RT}{\rho g M}$. Figure 5.1 shows the plot of the data. The slope of the line is 1.78 cm/(g dm^{-3}), so

$$\frac{RT}{\rho g M} = \frac{1.78\ \text{cm}}{\text{g dm}^{-3}} = 1.78\ \text{cm dm}^3\,\text{g}^{-1} = 1.78 \times 10^{-2}\ \text{m}^4\,\text{kg}^{-1}$$

Therefore,

$$M = \frac{RT}{(\rho g) \times (1.78 \times 10^{-2}\ \text{m}^4\,\text{kg}^{-1})}$$

$$= \frac{(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (293\ \text{K})}{(1.000 \times 10^3\ \text{kg m}^{-3}) \times (9.81\ \text{m s}^{-2}) \times (1.78 \times 10^{-2}\ \text{m}^4\,\text{kg}^{-1})} = \boxed{14.0\ \text{kg mol}^{-1}}$$

E5.15(b) Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*}\,[5.49] = \frac{0.02239\ \text{atm}}{0.02308\ \text{atm}} = \boxed{0.9701}$$

$$\gamma_A = \frac{a_A}{x_A} \text{ and } x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{920\ \text{g}}{18.02\ \text{g mol}^{-1}} = 51.1\ \text{mol} \qquad n_B = \frac{122\ \text{g}}{241\ \text{g mol}^{-1}} = 0.506\ \text{mol}$$

$$\text{So,} \quad x_A = \frac{51.1}{51.1 + 0.506} = 0.990 \quad \text{and} \quad \gamma_A = \frac{0.9701}{0.990} = \boxed{0.980}$$

5.16(b) In an ideal solution, the chemical potential of benzene would be

$$\mu = \mu^* + RT\ln x\ [5.22]$$

$$RT\ln x = (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times 353.3\ \mathrm{K} \times \ln 0.30 = \boxed{-3.5\times10^3\ \mathrm{J\ mol^{-1}}}.$$

Thus, its chemical potential is lowered by this amount.

$$p = ap^*\ [5.49] = \gamma x p^* = (0.93)\times(0.30)\times(760\ \mathrm{Torr}) = \boxed{212\ \mathrm{Torr}}.$$

Question. What is the lowering of the chemical potential in the non-ideal solution with $\gamma = 0.93$?

5.17(b) From Dalton's law of partial pressures and y_A we can compute the partial pressures:

$$y_A = \frac{p_A}{p_A + p_B} = \frac{p_A}{101.3\ \mathrm{kPa}} = 0.314$$

So, $p_A = 101.3\ \mathrm{kPa} \times 0.314 = 31.8\ \mathrm{kPa}$

and $p_B = 101.3\ \mathrm{kPa} - 31.8\ \mathrm{kPa} = 69.5\ \mathrm{kPa}$

$$a_A = \frac{p_A}{p_A^*} = \frac{31.8\ \mathrm{kPa}}{73.0\ \mathrm{kPa}} = \boxed{0.436} \quad \text{and} \quad a_B = \frac{p_B}{p_B^*} = \frac{69.5\ \mathrm{kPa}}{92.1\ \mathrm{kPa}} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A}\ [5.51] = \frac{0.436}{0.220} = \boxed{1.98} \quad \text{and} \quad \gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.967}$$

5.18(b) The definition of ionic strength is

$$I = \frac{1}{2}\sum_i \left(\frac{b_i}{b^\ominus}\right) z_i^2\ [5.76]$$

and if b is the molal concentration of an M_pX_q salt, the molal concentrations of the ions are

$$b_M = p \times b \quad \text{and} \quad b_X = q \times b$$

Hence, $I = \frac{1}{2}(pz_+^2 + qz_-^2)\left(\frac{b}{b^\ominus}\right)$

For $K_3[Fe(CN)_6]$ $I = \frac{1}{2}(3\times1^2 + 1\times3^2)\left(\frac{b}{b^\ominus}\right) = 6\left(\frac{b}{b^\ominus}\right)$

For KCl and NaBr (and any other compound of monovalent ions)

$$I = \frac{1}{2}(1\times1 + 1\times1)\left(\frac{b}{b^\ominus}\right) = \left(\frac{b}{b^\ominus}\right)$$

Thus, for this mixture

$$\begin{aligned} I &= I(K_3[Fe(CN)_6]) + I(KCl) + I(NaBr) \\ &= 6\left(\frac{b(K_3[Fe(CN)_6])}{b^\ominus}\right) + \frac{b(KCl)}{b^\ominus} + \frac{b(NaBr)}{b^\ominus} \\ &= (6)\times(0.040) + (0.030) + (0.050) = \boxed{0.320} \end{aligned}$$

COMMENT. Note that the strength of a solution of more than one electrolyte may be calculated by summing the ionic strengths of each electrolyte considered as a separate solution, as in the solution to this exercise, by summing the product $\frac{1}{2}\left(\frac{b_i}{b^\ominus}\right)z_i^2$ for each individual ion as in the definition of I [5.76].

Question. Can you establish that the comment holds for this exercise? Note that the term for K^+ in a sum over ions includes ions from two different salts.

E5.19(b) The original KNO_3 solution has an ionic strength of 0.110. (For compounds of monovalent ions, the ionic strength is numerically equal to the molal concentration, as shown in Exercise 5.18(b).) Therefore, the ionic strengths of the added salts must be 0.890.

(a) The salt to be added is monovalent, so an additional 0.890 mol kg^{-1} must be dissolved. The mass that must be added is therefore

$$(0.500\ \text{kg})\times(0.890\ \text{mol kg}^{-1})\times(101.11\ \text{g mol}^{-1})=\boxed{45.0\ \text{g}}$$

(b) For $Ba(NO_3)_2$ $\quad I=\frac{1}{2}(1\times 2^2+2\times 1^2)\left(\frac{b}{b^\ominus}\right)[5.76]=3\left(\frac{b}{b^\ominus}\right)$

Therefore, the solution should be made 0.890 mol kg^{-1}/3 = 0.297 mol kg^{-1} in $Ba(NO_3)_2$. The mass that should be added to 500 g of the solution is therefore

$$(0.500\ \text{kg})\times(0.297\ \text{mol kg}^{-1})\times(261.32\ \text{g mol}^{-1})=\boxed{38.8\ \text{g}}$$

E5.20(b) The solution is dilute, so use the Debye–Hückel limiting law:

$$\log\gamma_\pm=-|z_+z_-|AI^{1/2}\,[5.75]$$

$$I=\frac{1}{2}\sum_i\left(\frac{b_i}{b^\ominus}\right)z_i^2=\frac{1}{2}\{(0.020\times 1^2)+(0.020\times 1^2)+(0.035\times 2^2)+(2\times 0.035\times 1^2)\}$$
$$=0.125$$

For NaCl:

$$\log\gamma_\pm=-1\times 1\times 0.509\times(0.125)^{1/2}=-0.180,\quad \text{so}\quad \gamma_\pm=\boxed{0.66}$$

The activities of the ions are

$$a(Na^+)=a(Cl^-)=\gamma_\pm b/b^\circ=0.66\times 0.020=\boxed{0.013}$$

Question. What are the activity coefficients and activities of $Ca(NO_3)_2$ in the same solution?

E5.21(b) The extended Debye–Hückel law [eqn 5.78], with the parameter C set equal to zero, is

$$\log\gamma_\pm=-\frac{A|z_+z_-|I^{1/2}}{1+BI^{1/2}}$$

Solving for B:

$$B=-\left(\frac{1}{I^{1/2}}+\frac{A|z_+z_-|}{\log\gamma_\pm}\right)=-\left(\frac{1}{(b/b^\ominus)^{1/2}}+\frac{0.509}{\log\gamma_\pm}\right)$$

Draw up the following table:

$b/(\text{mol kg}^{-1})$	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
$\gamma_\pm$	0.927	0.902	0.816
B	1.32	1.36	1.29

The values of B are reasonably constant, illustrating that the extended law fits these activity coefficients with $B = \boxed{1.3}$.

5.22(b) Let subscript 2 denote the 1,2 isomer and 3 the 1,3 isomer. The partial pressures of the two liquids sum to 19 kPa:

$$p_3 + p_2 = p = x_3 p_3^* + x_2 p_2^* \text{ [Raoult's law]} = x_3 p_3^* + (1 - x_3)p_2^*$$

Solve for x_3:

$$x_3 = \frac{p - p_2^*}{p_3^* - p_2^*} = \frac{(19 - 20)\text{ kPa}}{(18 - 20)\text{ kPa}} = \boxed{0.5}$$

and $x_2 = 1 - 0.5 = \boxed{0.5}$

The vapour-phase mole fractions are given by Dalton's law:

$$y_3 = \frac{p_3}{p} = \frac{x_3 p_3^*}{p} = \frac{(0.5)\times 18\text{ kPa}}{19\text{ kPa}} = \boxed{0.4\overline{7}}$$

and $$y_2 = \frac{x_2 p_2^*}{p} = \frac{(0.5)\times 20.0\text{ kPa}}{519\text{ kPa}} = \boxed{0.5\overline{3}}.$$

5.23(b) The partial vapour pressures are given by Raoult's law:

$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^* = (1 - x_B)p_B^*$$

Dalton's law relates these vapour pressures to the vapour-phase mole fractions:

$$y_A = \frac{p_A}{p_\text{total}} = \frac{x_A p_A^*}{x_A p_A^* + (1 - x_A)p_B^*}$$

Solve for x_A:

$$x_A p_A^* + (1 - x_A)p_B^* = \frac{x_A p_A^*}{y_A}$$

$$x_A\left(p_A^* - p_B^* - \frac{p_A^*}{y_A}\right) = -p_B^*$$

$$x_A = \frac{p_B^*}{p_B^* + \frac{p_A^*}{y_A} - p_A^*} = \frac{82.1\text{ kPa}}{\left(82.1 + \frac{68.8}{0.621} - 68.8\right)\text{ kPa}} = \boxed{0.662}$$

and $x_B = 1 - x_A = 1 - 0.662 = \boxed{0.338}$

The total vapour pressure is

$$p_{\text{total}} = x_A p_A^* + x_B p_B^* = 0.662 \times 68.8\ \text{kPa} + 0.338 \times 82.1\ \text{kPa} = \boxed{73.3\ \text{kPa}}$$

E5.24(b) (a) If the solution is ideal, then the partial vapour pressures are given by Raoult's law:

$$p_A^\circ = x_A p_A^* = 0.4217 \times 110.1\ \text{kPa} = 46.4\ \text{kPa}$$

and $p_B^\circ = x_B p_B^* = (1 - x_B) p_B^* = (1 - 0.4217) \times 76.5\ \text{kPa} = 44.2\ \text{kPa}$

(Note the use of the symbol ° to emphasize that these are idealized quantities; we do not yet know if they are the actual partial vapour pressures.) At the normal boiling temperature, the partial vapour pressures must add up to 1 atm (101.3 kPa). These ideal partial vapour pressures add up to only 90.7 kPa, so the $\boxed{\text{solution is not ideal}}$.

(b) We actually do not have enough information to compute the initial composition of the vapour above the solution. The activities and activity coefficients are defined by the actual partial vapour pressures. We know only that the actual vapour pressures must sum to 101.3 kPa. We can make a further assumption that the proportions of the vapours are the same as given by Raoult's law. That is, we assume that

$$y_A = y_A^\circ = \frac{p_A^\circ}{p_A^\circ + p_B^\circ} = \frac{46.4\ \text{kPa}}{(46.4 + 44.2)\ \text{kPa}} = \boxed{0.512}$$

and $$y_B = y_B^\circ = \frac{p_B^\circ}{p_A^\circ + p_B^\circ} = \frac{44.2\ \text{kPa}}{(46.4 + 44.2)\ \text{kPa}} = \boxed{0.488}$$

By Dalton's law, the actual partial vapour pressures would then be

$$p_A = y_A p_{\text{total}} = 0.512 \times 101.3\ \text{kPa} = \boxed{51.9\ \text{kPa}}$$

and $p_B = y_B p_{\text{total}} = 0.488 \times 101.3\ \text{kPa} = \boxed{49.4\ \text{kPa}}$

To find the activity coefficients, note that

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{p_A}{p_A^\circ} = \frac{51.9\ \text{kPa}}{46.4\ \text{kPa}} = 1.117 \quad \text{and} \quad \gamma_B = \frac{49.4\ \text{kPa}}{44.2\ \text{kPa}} = 1.117$$

COMMENT. Assuming that the actual proportions of the vapours are the same as the ideal proportions arrives at the answer by conjecture rather than calculation. The assumption is not unreasonable, however. It is equivalent to assuming that the activity coefficients of the two components are equal (when in principle they could be different). Several facts combine to suggest that the error we make in making this assumption is fairly small: the difference between ideal and actual total pressure is relatively small (in the order of 10%), non-ideal behaviour is due to the *interaction* of the two components, and the two components are present in comparable quantities.

E5.25(b) (a) If the solution is ideal, then the partial vapour pressures are given by Raoult's law:

$$p_B = x_B p_B^* = 0.50 \times 9.9\ \text{kPa} = 4.95\ \text{kPa}$$

$$p_T = x_T p_T^* = 0.50 \times 2.9\ \text{kPa} = 1.45\ \text{kPa}$$

The total pressure is

$$p_{\text{total}} = p_B + p_T = (4.95 + 1.45)\ \text{kPa} = \boxed{6.4\ \text{kPa}}$$

(b) The composition of the vapour is given by

$$y_B = \frac{p_B}{p_{\text{total}}} = \frac{4.95\ \text{kPa}}{6.4\ \text{kPa}} = \boxed{0.77}$$

and $$y_T = \frac{p_T}{p_{\text{total}}} = \frac{1.45\ \text{kPa}}{6.4\ \text{kPa}} = \boxed{0.23}$$

(c) When only a few drops of liquid remain, the equimolar mixture is almost entirely vapour. Thus, $y_B = y_T = 0.50$, which implies that

$$p_B = x_B p_B^* = p_T = x_T p_T^* = (1 - x_B) p_T^*$$

Solving for x_B yields

$$x_B = \frac{p_T^*}{p_B^* + p_T^*} = \frac{2.9\ \text{kPa}}{(9.9 + 2.9)\ \text{kPa}} = 0.23$$

The partial vapour pressures are

$$p_B = x_B p_B^* = 0.23 \times 9.9\ \text{kPa} = 2.24\ \text{kPa} = p_T\ [\text{vapour mixture is equimolar}] = p_{\text{total}}/2$$

The total pressure is

$$p_{\text{total}} = 2p_B = \boxed{4.5\ \text{kPa}}$$

COMMENT. Notice that an equimolar liquid mixture yields a vapour composition directly proportional to the vapour pressures of the pure liquids. Conversely, an equimolar vapour mixture implies a liquid composition inversely proportional to those vapour pressures.

E5.26(b) Add the boiling point of A to the table at $x_A = y_A = 1$ and the boiling point of B at $x_B = y_B = 0$. Plot the boiling temperatures against liquid mole fractions and the same boiling temperatures against vapour mole fractions on the same plot.

The phase diagram is shown in Figure 5.2. The phase boundary curves are polynomial fits to the data points.

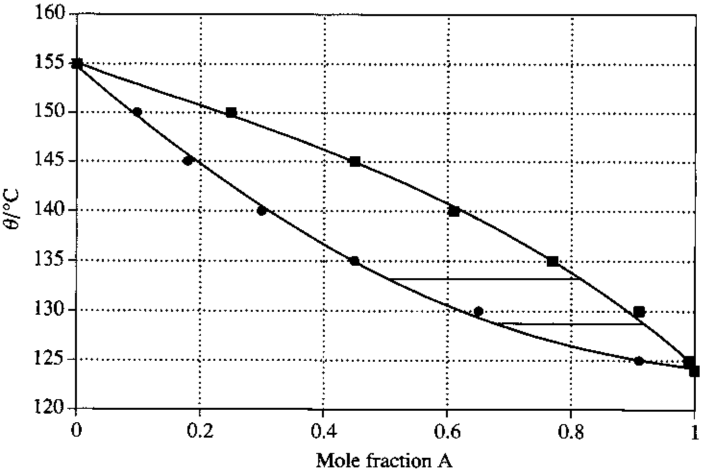


Figure 5.2

(a) Find $x_A = 0.50$ on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is $\boxed{y_A = 0.82}$.

(b) Find $x_A = 0.67$ (i.e. $x_B = 0.33$) on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is $\boxed{y_A = 0.91 \text{ (i.e. } y_B = 0.09)}$.

E5.27(b) The phase diagram is shown in Figure 5.3.

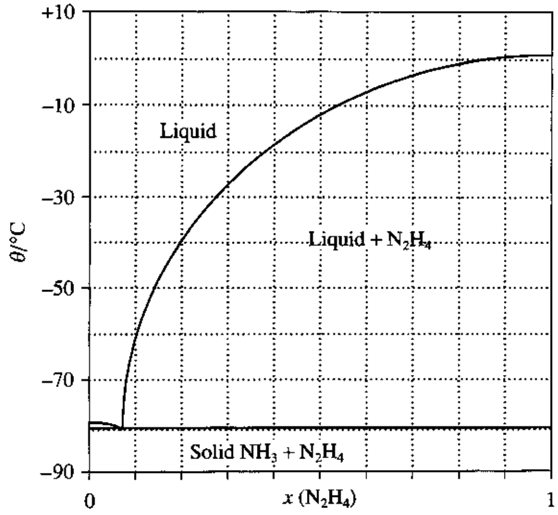


Figure 5.3

E5.28(b) See Figure 5.4 for labels.

(a) Solid Ag with dissolved Sn begins to precipitate at a_1, and the sample solidifies completely at a_2.

(b) Solid Ag with dissolved Sn begins to precipitate at b_1, and the liquid becomes richer in Sn as the temperature drops further. At b_2 solid Ag_3Sn begins to precipitate, and as cooling continues the liquid becomes richer in Sn. At b_3 the system has its eutectic composition (a solid solution of Sn and Ag_3Sn) and it freezes without further change in composition.

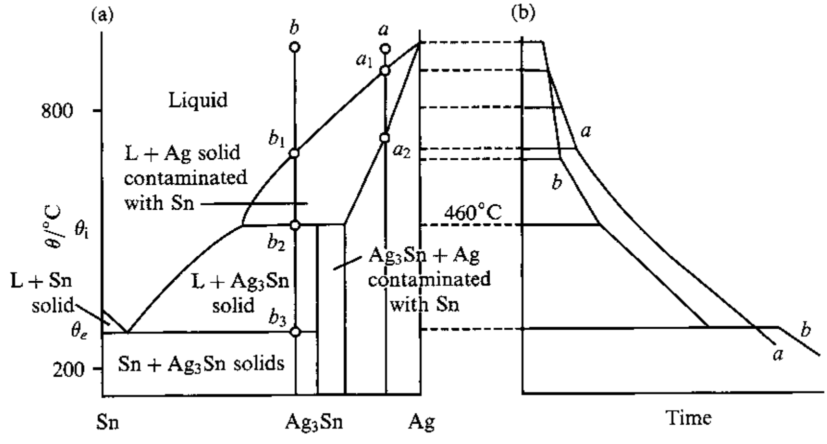


Figure 5.4

5.29(b) See Figure 5.5. The feature denoting incongruent melting is circled. There are two eutectics: one at $x_B = \boxed{0.59}$, $T = \boxed{T_2}$ and another at $x_B = \boxed{0.85}$, $T = \boxed{T_3}$.

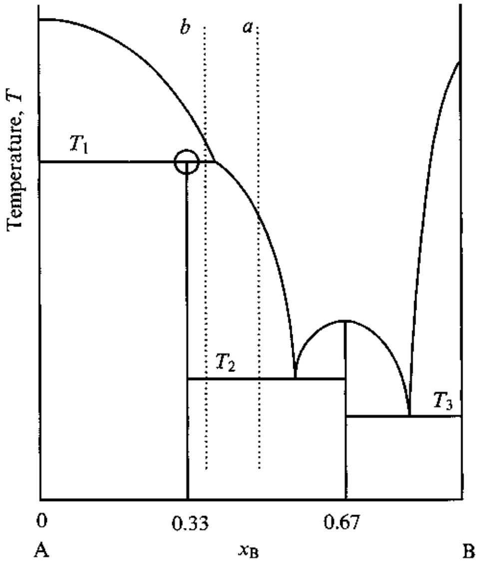


Figure 5.5

E5.30(b) The cooling curves corresponding to the phase diagram in Figure 5.6(a) are shown in Figure 5.6(b). Note the breaks (abrupt change in slope) at temperatures corresponding to points a_1, b_1, and b_2. Also, note the eutectic halts at a_2 and b_3.

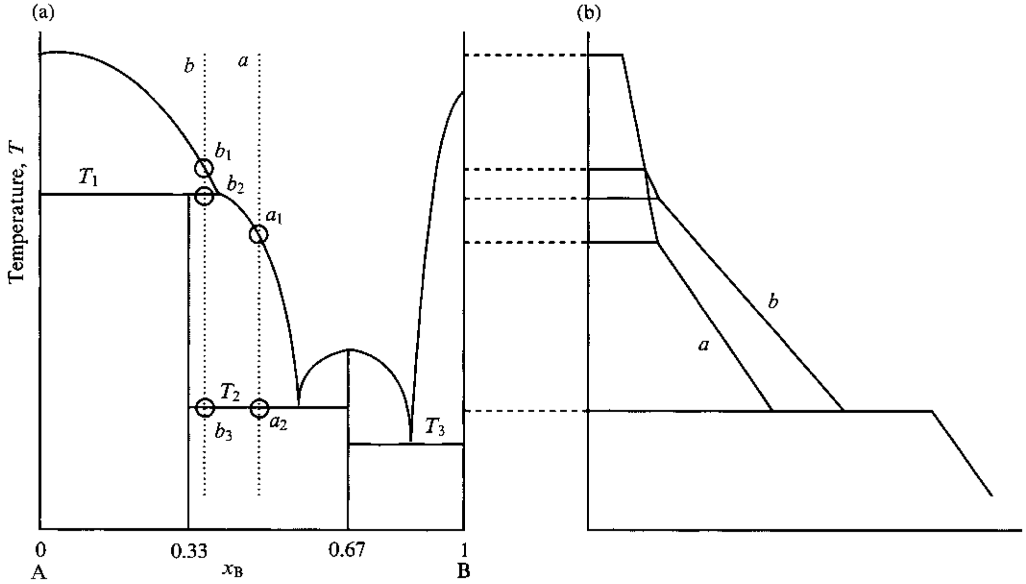


Figure 5.6(a) & (b)

E5.31(b) Refer to Figure 5.7. Horizontal lines have been drawn at the relevant temperatures.

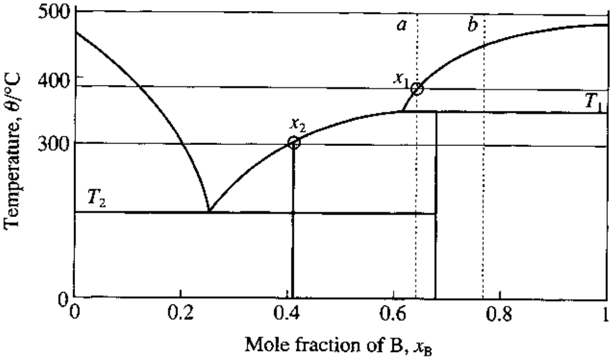


Figure 5.7

(a) At 390°C, solid B exists in equilibrium with a liquid whose composition is circled and labelled x_1 on Figure 5.7. That composition is $x_B = x_1 = 0.63$.

(b) At point x_2, two phases coexist: solid AB_2 and a liquid mixture of A and B with mole fraction $x_B = x_2 = 0.41$. Although the liquid does not contain any AB_2 units, we can think of the liquid as a mixture of dissociated AB_2 in A. Call the amount (moles) of the compound n_c and that of free A n_a. Thus, the amount of A (regardless of whether free or in the compound) is

$$n_A = n_a + n_c$$

and the amount of B is

$$n_B = 2n_c$$

The mole fraction of B is

$$x_B = x_2 = \frac{n_B}{n_A + n_B} = \frac{2n_c}{(n_a + n_c) + 2n_c} = \frac{2n_c}{n_a + 3n_c}$$

Rearrange this relationship, collecting terms in n_c on one side and n_a on the other:

$$n_a x_2 = n_c(2 - 3x_2)$$

The mole ratio of compound to free A is given by

$$\frac{n_c}{n_a} = \frac{x_2}{2 - 3x_2} = \frac{0.41}{2 - 3 \times 0.41} = \boxed{0.53}$$

5.32(b) The phase diagram is shown in Figure 5.8. Point symbols are plotted at the given data points. The lines are schematic at best.

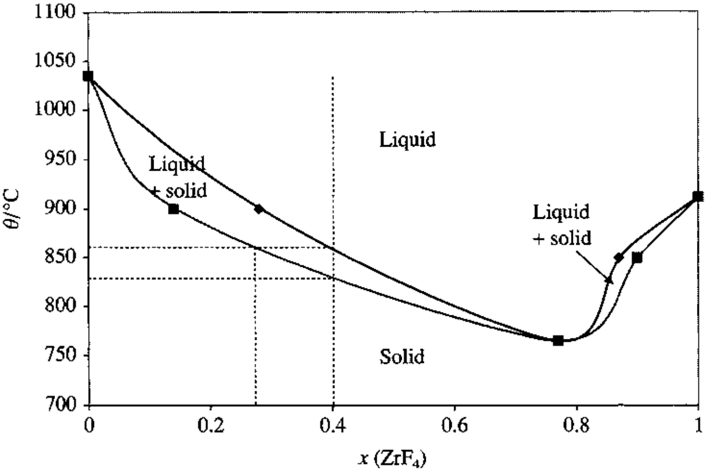


Figure 5.8

At 860°C, a solid solution with $x(\mathrm{ZrF_4}) = 0.27$ appears. The solid solution continues to form, and its $\mathrm{ZrF_4}$ content increases until it reaches $x(\mathrm{ZrF_4}) = 0.40$ at 830°C. At that temperature and below, the entire sample is solid.

E5.33(b) The phase diagram for this system (Figure 5.9) is very similar to that for the system methyl ethyl ether and diborane of Exercise 5.27(a). The regions of the diagram contain analogous substances. The mixture in this exercise has a diborane mole fraction of 0.80. Follow this isopleth down to see that crystallization begins at about 123 K. The liquid in equilibrium with the solid becomes progressively richer in diborane until the liquid composition reaches 0.90 at 104 K. Below that temperature the system is a mixture of solid compound and solid diborane.

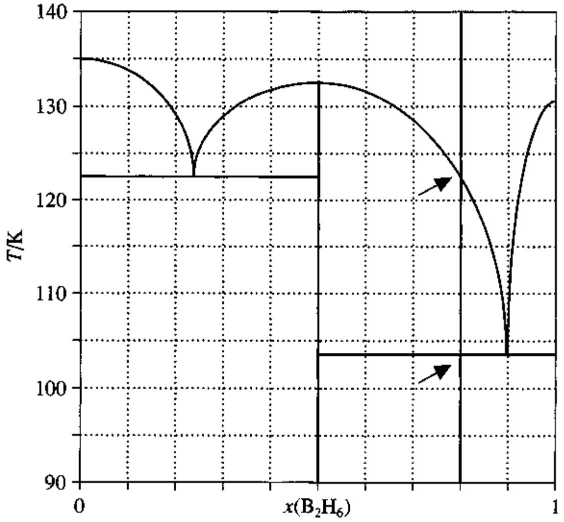


Figure 5.9

E5.34(b) The cooling curves are sketched in Figure 5.10. Note the breaks and halts. The breaks correspond to changes in the rate of cooling due to the freezing out of a solid that releases its heat of fusion and thus slows down the cooling process. The halts correspond to the existence of three phases and hence no variance until one of the phases disappears.

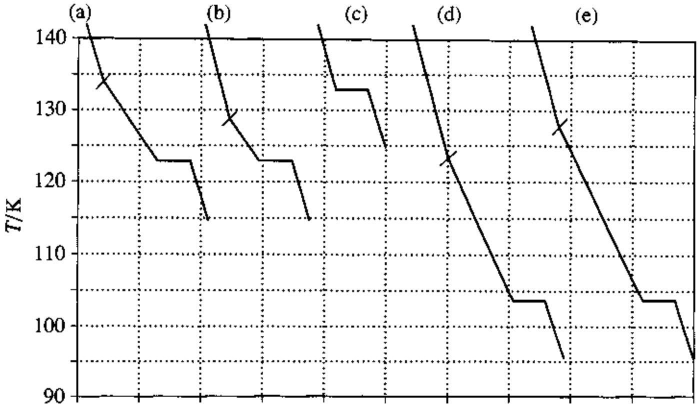


Figure 5.10

E5.35(b) The phase diagram is sketched in Figure 5.11.

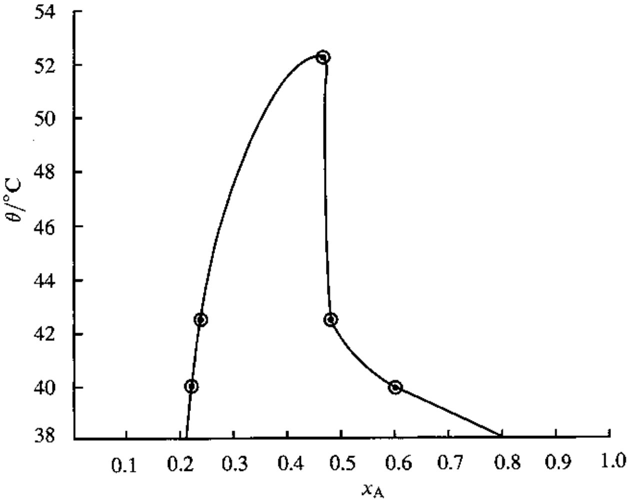


Figure 5.11

(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.

Solutions to problems

Solutions to numerical problems

5.2 Let A stand for water and B for NaCl(aq).

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{n_A} [5.1] = \left(\frac{\partial V}{\partial x}\right)_{n_A} \text{mol}^{-1}\ [x \equiv b/b^{\circ}]$$

$$= (16.62 + \tfrac{3}{2} \times 1.77 \times x^{1/2} + 2 \times 0.12x)\ \text{cm}^3\,\text{mol}^{-1}$$

$$= \boxed{17.5\ \text{cm}^3\,\text{mol}^{-1}}\ \text{when } x = 0.100$$

For a solution consisting of 0.100 mol NaCl and 1.000 kg water, corresponding to 55.49 mol H_2O, the total volume is given both by

$$V = \{1003 + 16.62 \times 0.100 + 1.77 \times (0.100)^{3/2} + 0.12 \times (0.100)^2\}\ \text{cm}^3 = 1004.\overline{7}\ \text{cm}^3$$

and by

$$V = V_A n_A + V_B n_B\ [5.3]$$

$$\text{Therefore, } V_A = \frac{V - V_B n_B}{n_A} = \frac{1004.\overline{7}\ \text{cm}^3 - (17.5\ \text{cm}^3) \times (0.100\ \text{mol})}{55.49\ \text{mol}} = \boxed{18.\overline{07}\ \text{cm}^3\,\text{mol}^{-1}}$$

COMMENT. To four figures, this result is the same as the molar volume of pure water at 25°C. (This agreement may be fortuitous, however, because the calculation does not give four significant figures.)

Question. How does the partial molar volume of NaCl(aq) in this solution compare to molar volume of pure solid NaCl?

P5.4 Letting B stand for $CuSO_4$(aq), the partial molar volume of the dissolved salt is

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{n_A} [5.1]$$

We will determine V_B by plotting V against n_B while holding n_A constant. We can find the volume from the density:

$$\rho = \frac{m_A + m_B}{V}, \quad \text{so} \quad V = \frac{m_A + m_B}{\rho}$$

The data include the composition of the solution expressed as mass per cent (that is, $m(CuSO_4)$/g, the mass in grams of B dissolved in 100 g solution, is numerically equal to w, defined as mass of B over total solution mass expressed as a percentage). For our plot, we need n_B per *fixed amount* of A. Let us choose that fixed quantity to be $m_A = 1$ kg exactly, so n_B is numerically equal to the molal concentration. So,

$$n_B = \frac{m_B}{M_B}$$

$$\text{such that } \frac{m_B}{m_A + m_B} \times 100 = w$$

Solve for m_B:

$$m_B = \frac{wm_A}{100 - w}$$

Draw up the following table of values of m_B, n_B, and V at each data point, using $m_A = 1000$ g:

w	5	10	15	20
$\rho/(\text{g cm}^{-3})$	1.051	1.107	1.167	1.23
m_B/g	52.6	111.1	176.5	250.0
n_B/mol	0.330	0.696	1.106	1.566
V/cm^3	1001.6	1003.7	1008.1	1016.3
$V_B/(\text{cm}^3\ \text{mol}^{-1})$	2.91	8.21	14.13	20.78

A plot V against n_B is shown in Figure 5.12.

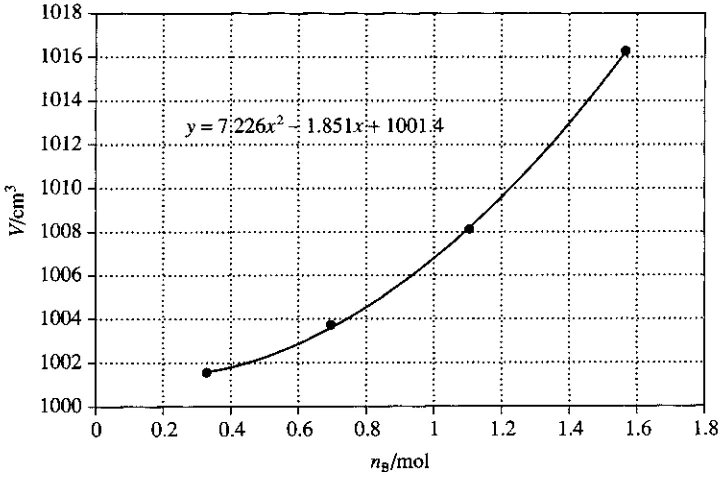


Figure 5.12

To find the partial molar volume, draw tangent lines to the curve at each of the data points and measure the slope of each tangent. Alternatively, fit the curve to a polynomial and differentiate the fit equation. A quadratic equation fits the data quite well

$$V/\text{cm}^3 = 7.226(n_B/\text{mol})^2 - 1.851(n_B/\text{mol}) + 1001.4$$

$$\text{so} \quad V_B/\text{cm}^3 = \left(\frac{\partial V/\text{cm}^3}{\partial n_B/\text{mol}}\right)_{n_A} = 2 \times 7.226 \times (n_B/\text{mol}) - 1.851$$

COMMENT. Selecting $m_A = 1000$ g is arbitrary. If you chose a different value for m_A, your table will have different values for m_B, n_B, and V, but you should arrive at the same values for V_B.

5.6 $$\Delta T = \frac{RT_f^{*2}x_B}{\Delta_{fus}H}\ [5.34], \quad x_B \approx \frac{n_B}{n_A} = \frac{n_B M_A}{1000\text{ g}}$$

Hence, $$\Delta T = \frac{n_B M_A RT_f^{*2}}{\Delta_{fus}H \times 1000\text{ g}} = \frac{bM_A RT_f^{*2}}{\Delta_{fus}H}\ [b\text{ is molality of solution}]$$

$$= b \times \left(\frac{(0.06005\text{ kg mol}^{-1}) \times (8.3145\text{ J K}^{-1}\text{mol}^{-1}) \times (290\text{ K})^2}{11.4 \times 10^3\text{ J mol}^{-1}}\right)$$

$$= 3.68\text{ K} \times b/(\text{mol kg}^{-1})$$

Thus, the apparent molality (based on measured freezing point depression) is

$$b_{app} = \frac{\Delta T}{3.68\text{ K}}\text{mol kg}^{-1} = \nu b$$

where b is the actual molality and ν may be interpreted as the number of ions in solution per one formula unit of KF. The apparent molar mass of KF can be determined from the apparent molality by the relationship

$$M_{B,app} = \frac{b}{b_{app}} \times M_B = \frac{1}{\nu} \times M_B = \frac{1}{\nu} \times (58.1\text{ g mol}^{-1})$$

where M_B is the actual molar mass of KF. We can draw up the following table from the data:

$b/(\text{mol kg}^{-1})$	0.015	0.037	0.077	0.295	0.602
$\Delta T/\text{K}$	0.115	0.295	0.470	1.381	2.67
$b_{app}/(\text{mol kg}^{-1})$	0.0312	0.0801	0.128	0.375	0.725
$\nu = b_{app}/b$	2.08	2.16	1.66	1.27	1.20
$M_{B,app}/(\text{g mol}^{-1})$	27.9	26.8	35.1	45.7	48.3

A possible explanation is that the dissociation of KF into ions is complete at the lower concentrations but incomplete at the higher concentrations. Values of ν greater than 2 are hard to explain, but they could be a result of the approximations involved in obtaining eqn 5.34. See the original reference for further information about the interpretation of the data.

5.8 (a) On a Raoult's law basis, $a = \frac{p}{p^*}$ [5.49] and $a = \gamma x$ [5.51], so $\gamma = \frac{p}{xp^*}$. On a Henry's law basis, $a = \frac{p}{K}$ [5.57], so $\gamma = \frac{p}{xK}$. The vapour pressures of the pure components are given in the table of data and are $p_I^* = 47.12$ kPa and $p_A^* = 37.38$ kPa.

(b) The Henry's law constant for iodoethane is determined by plotting the data and extrapolating the low concentration data to $x_I = 1$. (The Henry's law constant for ethyl acetate can also be determined by extrapolating the low-x_A data to $x_A = 1$, i.e. $x_I = 0$.) The data are plotted in Figure 5.13, and both Henry's law extrapolations are shown as dotted lines. The values obtained are $K_I = 64.4$ kPa and $K_A = 56.1$ kPa. (Note that the figure displays dashed lines, corresponding to Raoult's law in addition to the dotted Henry's law lines and the solid experimental curves.)

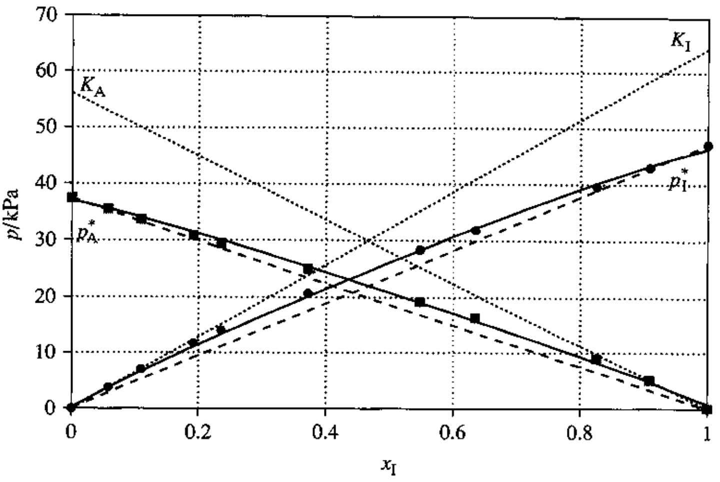


Figure 5.13

Then, draw up the following table based on the partial pressures given in the data:

x_I	0	0.0579	0.1095	0.1918	0.2353	0.3718
p_I/kPa	0	3.73	7.03	11.7	14.05	20.72
p_A/kPa	37.38[†]	35.48	33.64	30.85	29.44	25.05
γ_I(R)	—	1.367	1.362	1.295	1.267	1.183 $[p_I/x_I p_I^*]$
γ_A(R)	1.000	1.008	1.011	1.021	1.030	1.067 $[p_A/x_A p_A^*]$
γ_I(H)	1.000	1.000	0.997	0.947	0.927	0.865 $[p_I/x_I K_I]$

x_I	0.5478	0.6349	0.8253	0.9093	1
p_I/kPa	28.44	31.88	39.58	43	47.12[‡]
p_A/kPa	19.23	16.39	8.88	5.09	0
γ_I(R)	1.102	1.066	1.018	1.004	1
γ_A(R)	1.138	1.201	1.360	1.501	—
γ_I(H)	0.806	0.779	0.744	0.734	0.731

[†] The value of p_A^*; [‡] the value of p_I^*.

Question. In this problem both I and A were treated as solvents, but only I as a solute. Extend the table by including a row for γ_A(H).

P5.10 The partial molar volume of cyclohexane is

$$V_c = \left(\frac{\partial V}{\partial n_c}\right)_{n_p}$$

A similar expression holds for V_p. V_c can be evaluated graphically by plotting V against n_c (holding n_p constant) and finding the slope at the desired point. In a similar manner, V_p can be evaluated by plotting V against n_p. To find V_c, V is needed at a variety of n_c while holding n_p constant, say at exactly 1 mol; conversely, to find V_p, V is needed at a variety of n_p while holding n_c constant. The mole fraction in this system is

$$x_c = \frac{n_c}{n_c + n_p}, \quad \text{so} \quad n_c = \frac{x_c n_p}{1 - x_c} \quad \text{and} \quad n_p = \frac{(1 - x_c)n_c}{x_c}$$

From n_c and n_p, the mass of the sample can be calculated, and the volume can be calculated from

$$V = \frac{m}{\rho} = \frac{n_c M_c + n_p M_p}{\rho}$$

Draw up the following table, using $M_c = 84.16\ \mathrm{g\,mol^{-1}}$ and $M_p = 212.41\ \mathrm{g\,mol^{-1}}$. Note that the central columns are the given data. The columns on either side hold one component constant at 1 mol and compute the amount of the other component and the volume.

n_c/mol ($n_p = 1$)	V/cm^3	x_c	ρ/g cm^{-3}	n_p/mol ($n_c = 1$)	V/cm^3
2.295	529.4	0.6965	0.7661	0.4358	230.7
3.970	712.2	0.7988	0.7674	0.2519	179.4
9.040	1264	0.9004	0.7697	0.1106	139.9

These values are plotted in Figures 5.14(a) and (b).

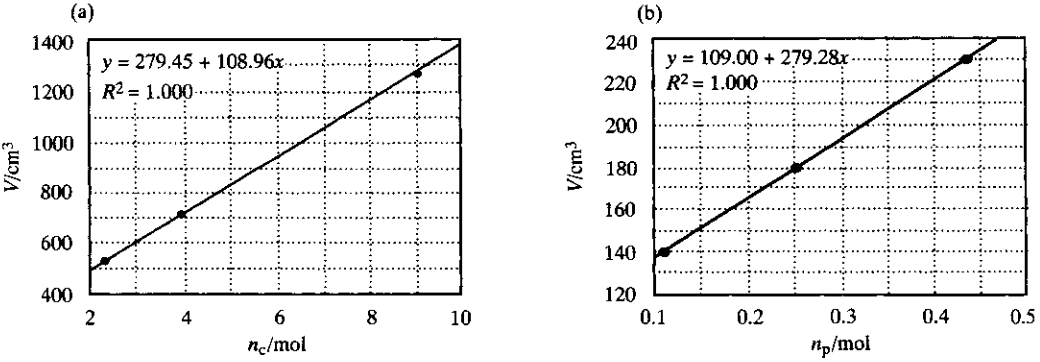


Figure 5.14(a) & (b)

These plots show no curvature, so in this case, perhaps due to the limited number of data points, the partial molar volumes are constant over the range of concentrations.

$$V_c = \boxed{109.0\ \mathrm{cm^3\,mol^{-1}}} \quad \text{and} \quad V_p = \boxed{279.3\ \mathrm{cm^3\,mol^{-1}}}$$

P5.12 The activity of a solvent is

$$a_A = \frac{p_A}{p_A^*}\ [5.49] = x_A \gamma_A\ [5.51]$$

so the activity coefficient is

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{y_A p}{x_A p_A^*}$$

where the last equality applies Dalton's law of partial pressures to the vapour phase. Since the data are given in terms of trichloromethane mole fractions, the last equation applies directly, changing subscript A to T. For the other component:

$$\gamma_E = \frac{y_E p}{x_E p_E^*} = \frac{(1-y_T)p}{(1-x_T)p_E^*}$$

Substituting the data yields the following table of results.

p/kPa	x_T	y_T	γ_T	γ_E
23.40	0.000	0.000	—	1.000
21.75	0.129	0.065	0.418	0.998
20.25	0.228	0.145	0.490	1.031
18.75	0.353	0.285	0.576	1.023
18.15	0.511	0.535	0.723	0.920
20.25	0.700	0.805	0.885	0.725
22.50	0.810	0.915	0.966	0.497
26.30	1.000	1.000	1.00	—

P5.14 $S = S_0 e^{\tau/T}$ may be written in the form $\ln S = \ln S_0 + \frac{\tau}{T}$, which indicates that a plot of ln S against $1/T$ should be linear with slope τ and intercept ln S_0. Linear regression analysis gives

$\tau = \boxed{165\ \text{K}}$ (standard deviation = 2 K)

$\ln(S_0/\text{mol dm}^{-3}) = 2.990$, standard deviation 0.007; $R = \boxed{0.99978}$

so the linear regression explains 99.98% of the variation.

$$S_0 = e^{2.990}\ \text{mol dm}^{-3} = \boxed{19.89\ \text{mol dm}^{-3}}$$

Eqn 5.37 gives the ideal solubility in mole fraction units:

$$x_B = \exp\left\{\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right)\right\} = \exp\left(\frac{\Delta_{\text{fus}}H}{RT_f}\right)\exp\left(-\frac{\Delta_{\text{fus}}H}{RT}\right)$$

Comparing the ideal expression to the empirical $S = S_0 e^{\tau/T}$ is not straightforward because of the different units. For dilute solutions, mole fraction and molarity are directly proportional:

$$x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} \quad \text{and} \quad [B] = \frac{n_B}{V_{\text{solution}}} \approx \frac{n_B}{V_A} = \frac{n_B \rho_A}{n_A M_A}$$

Clearly, however, the approximations involved here are not permissible for 20-molar solutions. At such high concentrations, n_B is not negligible compared to n_A; the amounts are comparable. Furthermore, the solution is surely much denser than the solvent. If the approximations *were* justified, however, we would identify S_0 with the temperature-independent part of eqn 5.37 and constants:

$$S_0 = \boxed{\frac{\rho_A}{M_A}\exp\left(\frac{\Delta_{\text{fus}}H}{RT_f}\right)}$$

Comparing the temperature-dependent portion, we would identify $\tau = \boxed{-\Delta_{\text{fus}}H/R}$. This identification is problematic. The empirical τ is positive, but so is $\Delta_{\text{fus}}H$. The empirical solubility decreases with increasing temperature, but the ideal solubility increases. That the ideal expression fails to capture the solubility behaviour of a highly concentrated ionic solution should not be surprising in light of Section 5.13.

.16 According to the Debye–Hückel limiting law

$$\log\gamma_{\pm} = -0.509\,|z_+z_-|\,I^{1/2}[5.75] = -0.509\left(\frac{b}{b^{\ominus}}\right)^{1/2}\ [5.76]$$

We draw up the following table:

b/(mmol kg^{-1})	1.0	2.0	5.0	10.0	20.0
$I^{1/2}$	0.032	0.045	0.071	0.100	0.141
$\gamma_{\pm}$(calc)	0.964	0.949	0.920	0.889	0.847
$\gamma_{\pm}$(exp)	0.9649	0.9519	0.9275	0.9024	0.8712
$\log\gamma_{\pm}$(calc)	−0.0161	−0.0228	−0.0360	−0.0509	−0.0720
$\log\gamma_{\pm}$(exp)	−0.0155	−0.0214	−0.0327	−0.0446	−0.0599

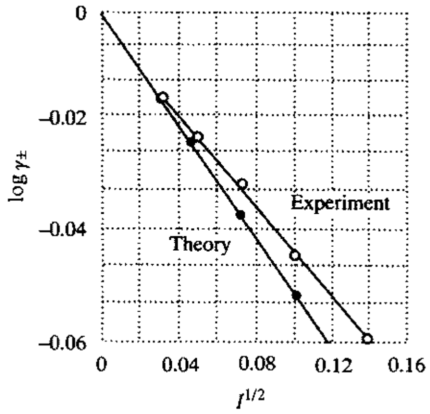


Figure 5.15

The points are plotted against $I^{1/2}$ in Figure 5.15. Note that the limiting slopes of the calculated and experimental curves coincide. A sufficiently good value of B in the extended Debye–Hückel law may be obtained by assuming that the constant A in the extended law is the same as A in the limiting law and taking $C = 0$.

$$\log\gamma_{\pm} = -\frac{A\,|z_+z_-|\,I^{1/2}}{1+BI^{1/2}}\ [5.78 \text{ with } C=0] = -\frac{AI^{1/2}}{1+BI^{1/2}}$$

Using the data at 20.0 mmol kg^{-1}, we may solve for B.

$$B = -\frac{A}{\log\gamma_{\pm}} - \frac{1}{I^{1/2}} = -\frac{0.509}{\log 0.8712} - \frac{1}{(20\times10^{-3})^{1/2}} = 1.43$$

Thus, $\log \gamma_{\pm} = -\dfrac{0.509 I^{1/2}}{1+1.43 I^{1/2}}$

In order to determine whether or not the fit is improved, we use the data at 10.0 mmol kg^{-1}:

$$\log \gamma_{\pm} = \frac{-(0.509)\times(0.100)}{(1)+(1.43)\times(0.100)} = -0.0445$$

which fits the data almost exactly. The fits to the other data points are also almost exact.

P5.18 (a) The phase diagram is shown in Figure 5.16.

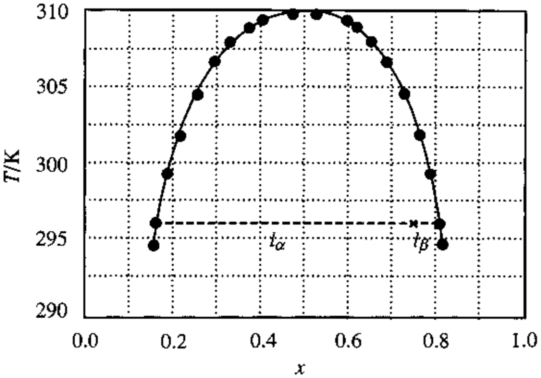


Figure 5.16

(b) We need not interpolate data, for 296.0 K is a temperature for which we have experimental data. The mole fraction of *N*, *N*-dimethylacetamide in the heptane-rich phase (call the point α, at the left of the tie line) is 0.168 and in the acetamide-rich phase (β, at right) 0.804. The proportions of the two phases are in an inverse ratio of the distance their mole fractions are from the composition point in question, according to the lever rule. That is

$$n_\alpha/n_\beta = l_\beta/l_\alpha = (0.804-0.750)/(0.750-0.168) = \boxed{0.093}$$

The smooth curve through the data crosses $x = 0.750$ at $\boxed{302.5\ \text{K}}$, the temperature at which the heptane-rich phase will vanish.

P5.20 The phase diagram is shown in Figure 5.17(a). The values of x_S corresponding to the three compounds are: (1) P_4S_3, 0.43; (2) P_4S_7, 0.64; (3) P_4S_{10}, 0.71.

The diagram has four eutectics labelled e_1, e_2, e_3, and e_4; eight two-phase liquid–solid regions, t_1 through t_8; and four two-phase solid regions, S_1, S_2, S_3, and S_4. The composition and physical state of the regions are as follows:

l: liquid S and P

S_1: solid P and solid P_4S_3

S_2: solid P_4S_3 and solid P_4S_7;

S_3: solid P_4S_7 and solid P_4S_{10}

S_4: solid P_4S_{10} and solid S

t_1: liquid P and S and solid P
t_2: liquid P and S and solid P_4S_3
t_3: liquid P and S and solid P_4S_3
t_4: liquid P and S and solid P_4S_7
t_5: liquid P and S and solid P_4S_7
t_6: liquid P and S and solid P_4S_{10}
t_7: liquid P and S and solid P_4S_{10}
t_8: liquid P and S and solid S

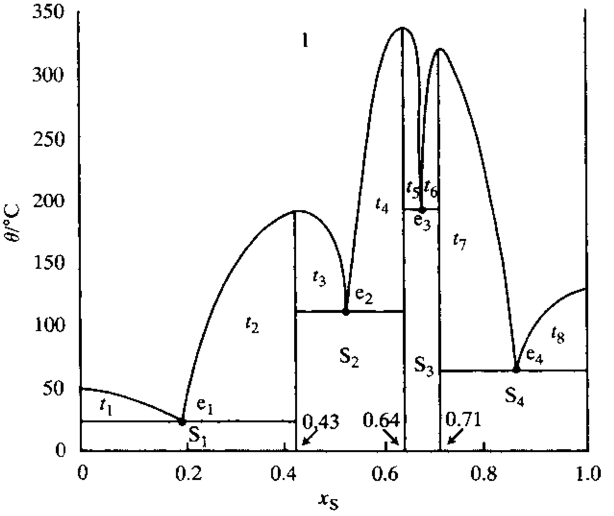


Figure 5.17(a)

A break in the cooling curve (Figure 5.17(b)) occurs at point $b_1 \approx 125°C$ as a result of solid P_4S_3 forming; a eutectic halt occurs at point $e_1 \approx 20°C$.

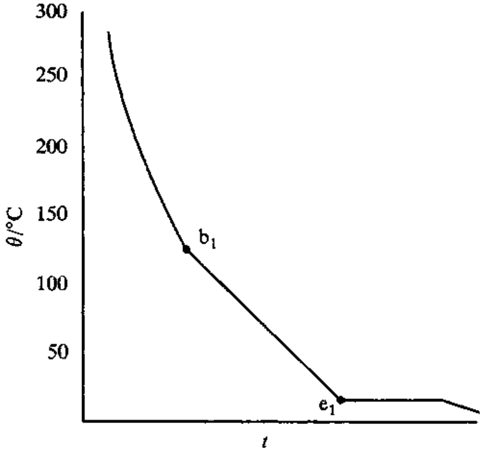


Figure 5.17(b)

P5.22 See Figure 5.18(a). The number of distinct chemical species (as opposed to components) and phases present at the indicated points are, respectively

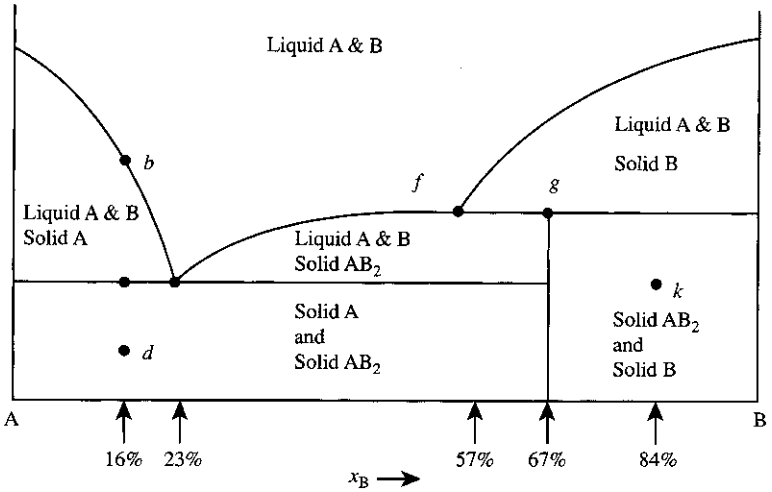


Figure 5.18(a)

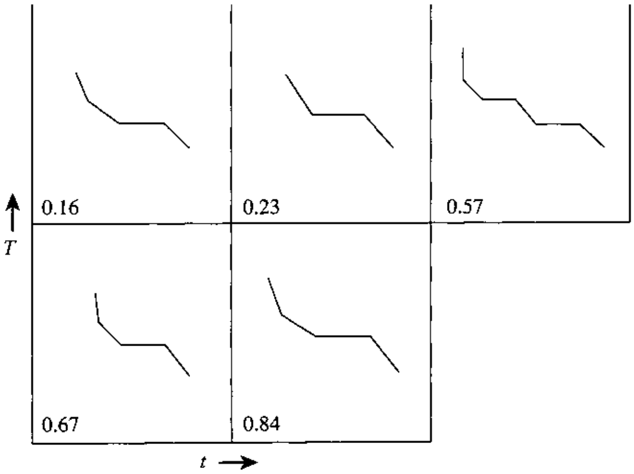


Figure 5.18(b)

b(3,2), *d*(2,2), *e*(4,3), *f*(4,3), *g*(4,3), *k*(2,2)

[Liquid A and solid A are here considered distinct species.]

The cooling curves are shown in Figure 5.18(b).

P5.24 (a) The $\Delta_{\text{mix}}G(x_{\text{Pb}})$ curves show that at 1500 K lead and copper are totally miscible. They mix to form a homogeneous solution no matter what the relative amounts may be. However, the curve at 1100 K displays two distinct minima, and we expect two partially miscible phases.

(i) $F = C - P + 2 = 2 - 1 + 2 = \boxed{3}$ at 1500 K

(ii) $F = C - P + 2 = 2 - 2 + 2 = \boxed{2}$ at 1100 K

(b)(i) When a homogeneous, equilibrium mixture with $x_B = x_{Pb} = 0.1$ is cooled from 1500 K to 1100 K, no phase separation occurs. The solution composition does not change.

(ii) When a homogeneous, equilibrium mixture with $x_{Pb} = 0.7$ is cooled slowly, two partially miscible phases appear somewhere between 1300 and 1100 K. The separation occurs because the composition lies between two minima on the $\Delta_{mix}G$ curve at 1100 K and phase separation lowers the total Gibbs energy. The composition of the two phases is determined by the equilibrium criterion $\mu_i(\alpha) = \mu_i(\beta)$ between the α and β phases. Since the chemical potential is the tangent of the $\Delta_{mix}G$ curve, we conclude that the straight line that is tangent to $\Delta_{mix}G(x)$ at two values of x (a double tangent) determines the composition of the two partially miscible phases. The two minima at 1100 K appear to have the same value of $\Delta_{mix}G$, namely -1 kJ mol^{-1}, so a horizontal line is tangent to both at the compositions $x_{Pb}(\alpha) = \boxed{0.19}$ and $x_{Pb}(\beta) = \boxed{0.82}$. (Note that the tangent points and the minima coincide in this case, but they need not. If the minima fall at different values of $\Delta_{mix}G$, then the line tangent to both of them is not horizontal and the points of tangency need not be the minima.) The relative amounts of the two phases are determined by the lever rule [eqn 5.46].

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha} = \frac{0.82 - 0.70}{0.70 - 0.19} = \boxed{0.24}$$

(c) Solubility at 1100 K is determined by the positions of the two minima in the $\Delta_{mix}G$ curve. The maximum amount of lead that can be dissolved in copper yields a mixture that has $x_{Pb} = 0.19$; any more lead produces a second phase. So, the solubility of lead in copper at this temperature is $\boxed{x_{Pb} = 0.19}$. The other minimum in the curve occurs at $x_{Pb} = 0.82$; any *less* lead produces a second phase. This lead-rich composition corresponds to the maximum solubility of copper in lead, namely $\boxed{x_{Cu} = 0.18}$.

Question. Express these solubilities in g solute per 100 g solvent.

5.26 The data are plotted in Figure 5.19. Compounds specified on the phase diagram are solids. Note that a few of the lines are slightly displaced so as to allow the smaller regions of the phase diagram to be visible. In particular, the intersection of the KCl and K_2FeCl_4 solubility curves is at a slightly greater $x(FeCl_2)$ than given in the problem in order to emphasize that it is not continuous with the vertical solid–solid phase boundary at $x = 0.33$. Likewise, the eutectic at 393°C and $x = 0.54$ is shown at a slightly lower temperature so as to distinguish it from the $KFeCl_3$ melting temperature. K_2FeCl_4 melts incongruently at 380°C and $KFeCl_3$ melts congruently at 399°C.

At $x = 0.36$, solid K_2FeCl_4 appears out of the single liquid phase at around 370°C. The solution becomes richer in $FeCl_2$ as more K_2FeCl_4 freezes out until the melt reaches the eutectic composition of 0.38 at 351°C, at which point $KFeCl_3(s)$ also appears. Below 351°C the system is a mixture of $K_2FeCl_4(s)$ and $KFeCl_3(s)$.

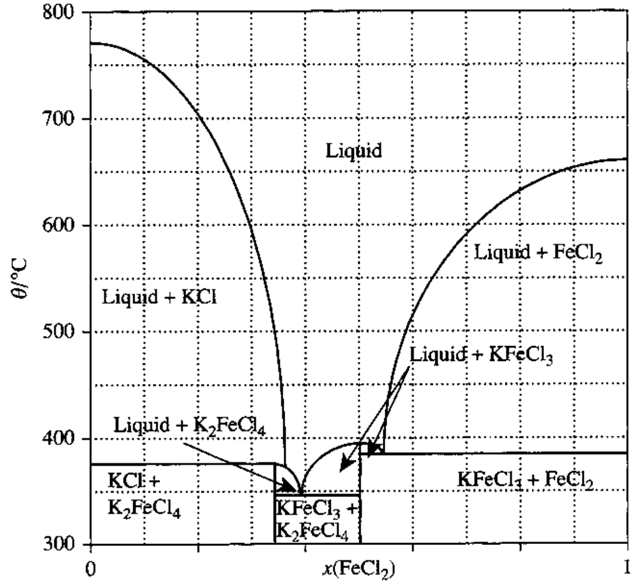


Figure 5.19

Solutions to theoretical problems

P5.28 Begin with the Gibbs–Duhem equation [5.12a] and divide through by total moles:

$$x_A\,d\mu_A + x_B\,d\mu_B = 0.$$

Dividing through by dx_A:

$$x_A\frac{d\mu_A}{dx_A} + x_B\frac{d\mu_B}{dx_A} = 0$$

The mole fractions add up to a constant (namely 1), so $dx_B = -dx_A$, and we can write

$$x_A\frac{d\mu_A}{dx_A} - x_B\frac{d\mu_B}{dx_B} = 0$$

$$(*)\quad \frac{d\mu_A}{d\ln x_A} = \frac{d\mu_B}{d\ln x_B}\left[d\ln x = \frac{dx}{x}\right].$$

Substitute the chemical potential of a real gas, namely

$$\mu = \mu^\ominus + RT\ln\frac{f}{p^\ominus} \text{ [5.14a with fugacity in place of pressure]},$$

into the starred equation, bearing in mind that the derivatives in it are really partial derivatives at constant p and T:

$$\left(\frac{\partial \ln f_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \ln f_B}{\partial \ln x_B}\right)_{p,T}$$

Now, go back to the starred equation and substitute into it the expression for chemical potential of a solvent in a solution, namely

$$\mu_A = \mu_A^* + RT\ln a_A \text{ [5.48]} = \mu_A^* + RT\ln\frac{p_A}{p_A^*} \text{ [5.49]},$$

yielding $\left(\dfrac{\partial \ln p_A}{\partial \ln x_A}\right)_{p,T} = \left(\dfrac{\partial \ln p_B}{\partial \ln x_B}\right)_{p,T}$

If A satisfies Raoult's law, we can write $p_A = x_A p_A^*$, which implies that

$$\left(\frac{\partial \ln p_A}{\partial \ln x_A}\right)_{p,T} = \frac{\partial \ln x_A}{\partial \ln x_A} + \frac{\partial \ln p_A^*}{\partial \ln x_A} = 1 + 0 = 1$$

which requires $\left(\dfrac{\partial \ln p_B}{\partial \ln x_B}\right)_{p,T} = 1$ as well. Both Raoult's law ($p_B = x_B p_B^*$) and Henry's law ($p_B = x_B K_B$) satisfy this requirement, as can be determined by differentiation. Indeed, Henry's law can be considered the more general of the two; Raoult's law can be considered a special case of Henry's law in which $K_B = p_B^*$.

P5.30 Start with eqn 5.33:

$$\mu_A^*(\mathrm{s}) = \mu_A^*(\mathrm{l}) + RT\ln x_A$$

Rearrange, analogous to *Justification* 5.1, to

$$\ln x_A = \frac{\mu_A^*(\mathrm{s}) - \mu_A^*(\mathrm{l})}{RT} = \frac{-\Delta_{\mathrm{fus}}G}{RT}$$

So, $\dfrac{\mathrm{d}\ln x_A}{\mathrm{d}T} = -\dfrac{1}{R}\times\dfrac{\mathrm{d}}{\mathrm{d}T}\left(\dfrac{\Delta_{\mathrm{fus}}G}{T}\right) = \boxed{\dfrac{\Delta_{\mathrm{fus}}H}{RT^2}}$ [Gibbs–Helmholtz equation, 3.55]

Integration yields

$$\int_1^{x_A} \mathrm{d}\ln x_A = \int_{T^*}^{T} \frac{\Delta_{\mathrm{fus}}H\mathrm{d}T}{RT^2} \approx \frac{\Delta_{\mathrm{fus}}H}{R}\int_{T^*}^{T}\frac{\mathrm{d}T}{T^2}$$

or $\boxed{\ln x_A = \dfrac{-\Delta_{\mathrm{fus}}H}{R}\times\left(\dfrac{1}{T} - \dfrac{1}{T^*}\right)}$

The approximations $\ln x_A = \ln(1 - x_B) \approx -x_B$ and $T \approx T^*$ then lead to eqns 5.34 here, just as (in *Justification* 5.1) they lead to eqn 5.31.

5.32 Retrace the argument in *Justification* 5.3, leading to eqn 5.38 of the text. Exactly the same process applies with a_A in place of x_A. At equilibrium

$$\mu_A^*(p) = \mu_A(a_A, p+\Pi) = \mu_A^*(p+\Pi) + RT\ln a_A = \mu_A^*(p) + \int_p^{p+\Pi} V_m\mathrm{d}p + RT\ln a_A$$

which implies that $\displaystyle\int_p^{p+\Pi} V_m\mathrm{d}p = -RT\ln a_A$.

For an incompressible solution, the integral evaluates to ΠV_m, so $\Pi V_m = -RT \ln a_A$.

In terms of the osmotic coefficient ϕ (Problem 5.31)

$$\Pi V_m = r\phi RT, \quad \text{where} \quad r = \frac{x_B}{x_A} = \frac{n_B}{n_A} \quad \phi = -\frac{x_A}{x_B}\ln a_A = -\frac{1}{r}\ln a_A$$

For a dilute solution, $V = nV_m \approx n_A V_m$

Hence, $\Pi V = n_B \phi RT$

and therefore, with $[B] = \frac{n_B}{V}$, $\boxed{\Pi = \phi[B]RT}$.

Solutions to applications

P5.34 The 97% saturated haemoglobin in the lungs releases oxygen in the capillary until the haemoglobin is 75% saturated.

100 cm^3 of blood in the lung containing 15.0 g of Hb at 97% saturated with O_2 binds

$$1.34\ \text{cm}^3\ \text{g}^{-1} \times 15.0\ \text{g} = 20.1\ \text{cm}^3\ O_2$$

The same 100 cm^3 of blood in capillaries would contain

$$20.1\ \text{cm}^3\ O_2 \times \frac{75\%}{97\%} = 15.5\ \text{cm}^3$$

Therefore, about (20.1 − 15.5) cm^3 or $\boxed{4.6\ \text{cm}^3}$ of O_2 is given up in the capillaries to body tissue.

P5.36 (a) Implicit in the model we are exploring is that at most one small molecule A can bind to each macromolecule, so the species are limited to free A, free M, and MA (no MA_2, etc.). In that case, the average number bound is also equal to the fraction of macromolecules that are bound to small molecules. Therefore, $[MA] = \nu[M]$, where [M] is the total concentration of M, bound and unbound. Similarly, $[M]_{\text{free}} = (1-\nu)[M]$. Therefore,

$$K = \frac{[MA]}{[M]_{\text{free}}[A]_{\text{free}}} = \frac{\nu[M]}{(1-\nu)[M][A]_{\text{free}}} = \frac{\nu}{(1-\nu)[A]_{\text{out}}},$$

where we use $[A]_{\text{free}} = [A]_{\text{out}}$ in the last step.

(b) At the risk of introducing more notation, let us rewrite the binding equilibrium in terms of individual binding sites, S:

$$S + A \rightleftharpoons SA,$$

for which the equilibrium constant is

$$K = \frac{[SA]}{[S]_{\text{free}}[A]_{\text{free}}}$$

The concentration of bound sites is the average number per site times the number of sites per macromolecule times the total concentration of macromolecules:

$$[SA] = (\nu/N)N[M] = \nu[M]$$

Similarly, the concentration of free sites is

$$[\mathrm{S}]_{\text{free}} = (1 - \nu/N)N[\mathrm{M}] = (N - \nu)[\mathrm{M}].$$

Thus, $K = \dfrac{\nu[\mathrm{M}]}{(N - \nu)[\mathrm{M}][\mathrm{A}]_{\text{out}}}$,

which rearranges to the Scatchard equation

$$KN - \nu K = \frac{\nu}{[\mathrm{A}]_{\text{out}}}$$

(c) The requisite plot is of $\nu/[\mathrm{EB}]_{\text{out}}$ vs. ν. If the Scatchard equation applies, the points should fall on a straight line with slope $-K$ and y-intercept KN. Use

$$v = \frac{[\mathrm{EB}]_{\text{bound}}}{[\mathrm{M}]} \quad \text{and} \quad [\mathrm{EB}]_{\text{bound}} = [\mathrm{EB}]_{\text{in}} - [\mathrm{EB}]_{\text{out}}$$

to draw up the following table:

$[\mathrm{EB}]_{\text{out}}/(\mu\text{mol dm}^{-3})$	0.042	0.092	0.204	0.526	1.150
$[\mathrm{EB}]_{\text{bound}}/(\mu\text{mol dm}^{-3})$	0.250	0.498	1.000	2.005	3.000
ν	0.250	0.498	1.000	2.005	3.000
$(\nu/[\mathrm{EB}]_{\text{out}})/(\text{dm}^3\,\mu\text{mol}^{-1})$	5.95	5.41	4.90	3.81	2.61

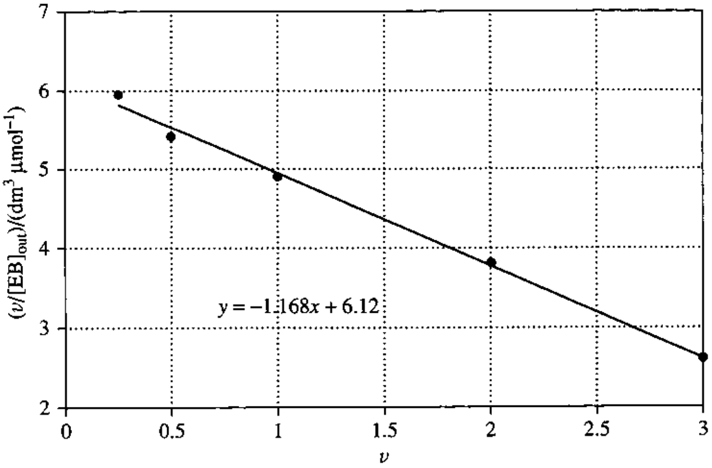


Figure 5.20

A plot of $\nu/[\mathrm{EB}]_{\text{out}}$ against ν is shown in Figure 5.20.

The slope is $-1.168\ \text{dm}^3\,\mu\text{mol}^{-1} = -1.168 \times 10^6\ \text{dm}^3\,\text{mol}^{-1}$, hence $K = \boxed{1.168 \times 10^6}$. (Note that K is conventionally defined as a dimensionless quantity when concentrations are given in mol dm^{-3}, but one can specify units and say $K = 1.167\ \text{dm}^3\,\mu\text{mol}^{-1}$. The intercept at $\nu = 0$ is

$$KN = 6.12\ \text{dm}^3\,\mu\text{mol}^{-1}, \quad \text{so} \quad N = \boxed{5.23}$$

and this is the average number of binding sites per oligonucleotide. The close fit of the data to a straight line indicates that the identical and independent sites $\boxed{\text{is applicable}}$.

P5.38 $PX_\upsilon(s) \rightleftharpoons P^{\upsilon+}(aq) + \upsilon X^-(aq)$

This process is a solubility equilibrium described by a solubility constant K_s:

$$K_s = a_P \times a_X^\upsilon$$

Introducing activity coefficients and concentrations, b, we obtain

$$K_s = b_P \times b_X^\upsilon \times \gamma_\pm^{\upsilon+1}$$

At low to moderate ionic strengths we can use the Debye–Hückel limiting law [eqn 5.75] as a good approximation for $\gamma_\pm$:

$$\log \gamma_\pm = -|z_- z_+| A I^{1/2}$$

Addition of a salt, such as $(NH_4)_2SO_4$, causes I to increase, $\log \gamma_\pm$ to become more negative, and $\gamma_\pm$ to decrease. However, K_s is a true equilibrium constant and remains unchanged. Therefore, the concentration of $P^{\upsilon+}$ increases and the protein solubility increases proportionately.

We may also explain this effect in terms of Le Chatelier's principle. As the ionic strength increases by the addition of an inert electrolyte such as $(NH_4)_2SO_4$, the ions of the protein that are in solution attract one another less strongly, so that the equilibrium is shifted in the direction of increased solubility.

The explanation of the salting out effect is somewhat more complicated and can be related to the failure the Debye–Hückel limiting law at higher ionic strengths. At high ionic strengths we may write the extended Debye–Hückel law [eqn 5.78]

$$\log \gamma_\pm = \frac{-|z_+ z_-| A I^{1/2}}{1 + B I^{1/2}} + CI$$

At low concentrations of inert salt, $I^{1/2} > I$, the first term dominates, $\gamma_\pm$ decreases with increasing I, and salting in occurs, but at high concentrations, $I > I^{1/2}$, the second term dominates, $\gamma_\pm$ increases with increasing I, and salting out occurs. The Le Chatelier's principle explanation is that the water molecules are tied up by ion–dipole interactions and become unavailable for solvating the protein, thereby leading to decreased solubility.

P5.40 We use eqn 5.40 in the form given in Example 5.4 with $\Pi = \rho g h$, then

$$\frac{\Pi}{c} = \frac{RT}{M}\left(1 + \frac{B}{M}c\right) = \frac{RT}{M} + \frac{RTB}{M^2}c$$

where c is the mass concentration of the polymer. Therefore, plot Π/c against c. The intercept is RT/M and the slope is RTB/M^2.

The transformed data to plot are given in the table:

$c/(\text{mg cm}^{-3})$	1.33	2.10	4.52	7.18	9.87
$(\Pi/c)/(\text{N m}^{-2}\text{ mg}^{-1}\text{ cm}^3)$	22.6	24.3	29.2	34.3	39.5

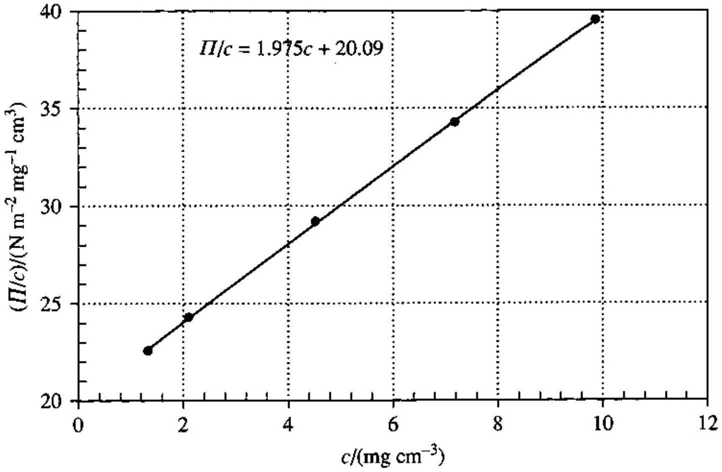


Figure 5.21

The plot is shown in Figure 5.21. The intercept is 20.1 $\mathrm{N\,m^{-2}/(mg\,cm^{-3})}$. The slope is 1.975 $\mathrm{N\,m^{-2}/(mg\,cm^{-3})^2}$. Therefore,

$$\begin{aligned}
M &= \frac{RT}{20.1\ \mathrm{N\,m^{-2}\,mg^{-1}\,cm^{3}}} \\
&= \frac{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 303.15\ \mathrm{K}}{20.1\ \mathrm{J\,m^{-3}\,mg^{-1}\,cm^{3}}} \times \left(\frac{10^{-3}\ \mathrm{g}}{1\ \mathrm{mg}}\right) \times \left(\frac{1\ \mathrm{cm}}{10^{-2}\ \mathrm{m}}\right)^{3} \\
&= \boxed{1.25 \times 10^{5}\ \mathrm{g\,mol^{-1}}}
\end{aligned}$$

$$\begin{aligned}
B &= \frac{M^{2}}{RT} \times 1.975\ \mathrm{N\,m^{-2}/(mg\,cm^{-3})^{2}} \\
&= \frac{M}{\left(\dfrac{RT}{M}\right)} \times 1.975\ \mathrm{N\,m^{-2}/(mg\,cm^{-3})^{2}} \\
&= \frac{1.25 \times 10^{5}\ \mathrm{g\,mol^{-1}} \times 1.975\ \mathrm{N\,m^{-2}/(mg\,cm^{-3})^{2}}}{20.1\ \mathrm{N\,m^{-2}/(mg\,cm^{-3})}} \times \frac{1\ \mathrm{mg}}{10^{-3}\ \mathrm{g}} \\
&= 1.23 \times 10^{7}\ \mathrm{cm^{3}\,mol^{-1}} = \boxed{1.23 \times 10^{4}\ \mathrm{dm^{3}\,mol^{-1}}}
\end{aligned}$$

5.42 Kevlar is a polyaromatic amide. Phenyl groups provide aromaticity and a planar, rigid structure. The amide group is expected to be like the peptide bond that connects amino acid residues within protein molecules. This group is also planar because resonance produces partial double-bond character between the carbon and nitrogen atoms. There is a substantial energy barrier preventing free rotation about the CN bond. The two bulky phenyl groups on the ends of an amide group are *trans* because steric hinderance makes the *cis* conformation unfavourable. See Figure 5.22(a).

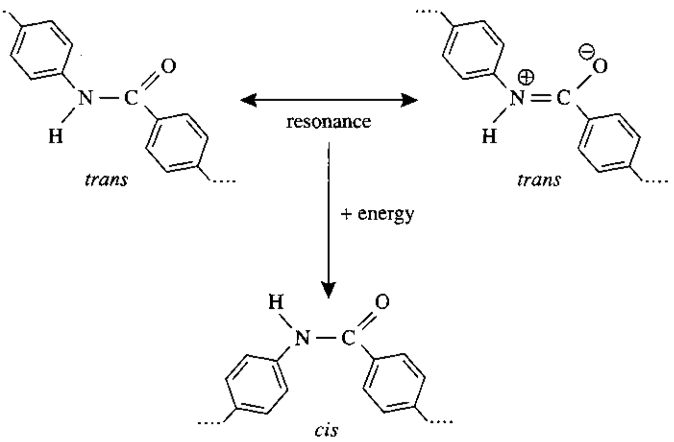


Figure 5.22(a)

The flatness of the Kevlar polymeric molecule makes it possible to process the material so that many molecules with parallel alignment form highly ordered, untangled crystal bundles. The alignment makes possible both considerable van der Waals attractions between adjacent molecules and for strong hydrogen bonding between the polar amide groups on adjacent molecules. These bonding forces create the high thermal stability and mechanical strength observed in Kevlar. See Figure 5.22(b).

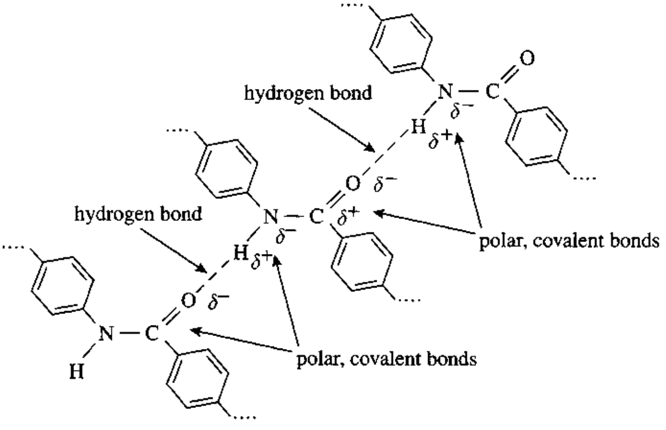


Figure 5.22(b)

Kevlar is able to absorb great quantities of energy, such as the kinetic energy of a speeding bullet, through hydrogen-bond breakage and the transition to the *cis* conformation.

6 Chemical equilibrium

Answers to discussion questions

D6.2 Eqn 5.56, in the form of the following expression, provides the general definition of the **activity** for species J, a_J:

$$\mu_J = \mu_J^{\ominus} + RT\ln a_J \ [5.56]$$

where $\mu_J^{\ominus}$ is the value of the chemical potential of J in the standard state, i.e. the state for which $a_J = 1$. In fact, the **standard state** of a substance at a specified temperature is its pure form at 1 bar. This means that the activity of a substance that is a either a pure solid (e.g. copper, sodium chloride, naphthalene) or a pure liquid (e.g. bromine, water, methanol) equals 1 at, say, 25°C. Since the activity of a pure solid or liquid is equal to 1, it can be conveniently ignored when presenting an equilibrium constant expression.

Activities and **activity coefficients** are generally used to address questions that concern real, non-ideal mixtures. It is well worth remembering several useful activity forms. Of course, both activities, a_J, and activity coefficients, γ_J, of non-ideal mixtures are dimensionless and related by equations that have the general form $a_J = \gamma_J \times$ (concentration of J).

Perfect gas:	$a_J = p_J/p^{\ominus}$	($\mu_J^{\ominus}$ depends on T alone; $p^{\ominus} \equiv 1$ bar)
Real gas:	$a_J = \gamma_J p_J/p^{\ominus}$	($\mu_J^{\ominus}$ depends on T alone)
Ideal solutions:	$a_J = x_J$	
Ideal-dilute solutions:	$a_B = [B]/c^{\ominus}$, where $c^{\ominus} \equiv 1$ mol dm^{-3}	
Solvent A of a non-ideal solution:	$a_A = \gamma_A x_A$	
Solute B of a non-ideal solution:	$a_B = \gamma_B[B]/c^{\ominus}$	

.4 (1) Response to change in pressure. The equilibrium constant is independent of pressure, but the individual partial pressures of a gas-phase reaction can change as the total pressure changes. This will happen when there is a difference, $\Delta\nu$, between the sums of the number of moles of gases on the product and reactant sides of the balanced chemical reaction equation.

$$\Delta\nu = \sum_J \nu_J = \sum_{J=\text{product gases}} \nu_J - \sum_{J=\text{reactant gases}} |\nu_J|$$

The requirement of an unchanged equilibrium constant implies that the side with the smaller number of moles of gas be favoured as pressure increases. To see this, we examine the general reaction equation $0 = \sum_J \nu_J J$ [6.9] in the special case for which all reactants and products are perfect gases. In this case, the activities equal the partial pressure of the gaseous species and, therefore,

$$a_{J(\text{gas})} = p_J/p^\ominus = x_J p/p^\ominus$$

where x_J is the mole fraction of gaseous species J. Substitution into eqn 6.13 and simplification yields a useful equation:

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J x_J^{\nu_J}(p/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= \left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}} \left(\prod_J (p/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}} (p/p^\ominus)^{\Delta\nu}$$

$$= K_x(p/p^\ominus)^{\Delta\nu}, \quad \text{where} \quad K_x = \left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}}$$

K_x is not an equilibrium constant. It is a ratio of product and reactant concentration factors that has a form analogous to the equilibrium constant K. However, whereas K depends on temperature alone, the concentration ratio K_x depends on both temperature and pressure. Solving for K_x provides an equation that directly indicates its pressure dependence:

$$K_x = K(p/p^\ominus)^{-\Delta\nu}$$

This equation indicates that, if $\Delta\nu = 0$ (an equal number of gas moles on both sides of the balanced reaction equation), $K_x = K$ and the concentration ratio has no pressure dependence. An increase in pressure causes no change in K_x and no shift in the concentration equilibrium is observed on a change in pressure.

However, this equation indicates that, if $\Delta\nu < 0$ (fewer moles of gas on the product side of the balanced reaction equation), $K_x = K(p/p^\ominus)^{|\Delta\nu|}$. Because p is raised to a positive power in this case, an increase in pressure causes K_x to increase. This means that the numerator concentrations (products) must increase while the denominator concentrations (reactants) decrease. The concentrations shift to the product side to re-establish equilibrium when an increase in pressure has stressed the reaction equilibrium. Similarly, if $\Delta\nu > 0$ (fewer moles of gas on the reactant side of the balanced reaction equation), $K_x = K(p/p^\ominus)^{-|\Delta\nu|}$. Because p is raised to a negative power in this case, the concentrations now shift to the reactant side to re-establish equilibrium when an increase in pressure has stressed the reaction equilibrium.

(2) Response to change in temperature. The **van 't Hoff equation,** $\dfrac{\mathrm{d}\ln K}{\mathrm{d}T} = \dfrac{\Delta_r H^\ominus}{RT^2}$ [6.21(a)], shows that K decreases with increasing temperature when the reaction is exothermic (i.e. $\Delta_r H^\ominus < 0$); thus the reaction shifts to the left. The opposite occurs in endothermic reactions (i.e. $\Delta_r H^\ominus > 0$). See Section 6.4 for a more detailed discussion.

D6.6 On a very basic level we observe that a concentration gradient establishes a chemical-potential gradient and it is the potential gradient that can generate an electric current. The extreme example is provided by the **electrolyte concentration cell,** which is by definition a galvanic cell consisting of two electrodes of the same metal in different concentration of the same salt of that metal. The concentration cell having two $M^+(aq)/M$ electrodes is $M(s)|M^+(aq,L)||M^+(aq,R)|M(s)$ and the net reaction is $M^+(aq,R) \rightarrow M^+(aq,L)$. For such a cell $E^\ominus_{\text{cell}} = 0$ and the Nernst equation gives the cell potential:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{\nu F}\ln Q\,[6.27] = -\frac{RT}{F}\ln\frac{a_{\text{M}^+(\text{L})}}{a_{\text{M}^+(\text{R})}}$$

With $[\text{M}^+(\text{R})] = 10 \times [\text{M}^+(\text{L})]$ and an assumption that $\gamma_{\text{M}^+(\text{L})} \approx \gamma_{\text{M}^+(\text{R})}$:

$$E_{\text{cell}} = -(25.693\text{ mV}) \times \left(\ln\frac{1}{10}\right) = 59.16\text{ mV}$$

The cell potential is half as large for the $\text{M(s)}|\text{M}^{2+}(\text{aq,L})||\text{M}^{2+}(\text{aq,R})|\text{M(s)}$ cell.

D6.8 The pH of an aqueous solution can in principle be measured with any electrode having an emf that is sensitive to $\text{H}^+(\text{aq})$ concentration (activity). In principle, the hydrogen gas electrode is the simplest and most fundamental. A cell is constructed with the hydrogen electrode being the right-hand electrode and any reference electrode with known potential as the left-hand electrode. A common choice is the saturated calomel electrode. The pH can then be obtained by measuring the emf (zero-current potential difference), E_{cell}, of the cell. The hydrogen gas electrode is not convenient to use, so in practice glass electrodes are used because of ease of handling (see Impact 6.3).

Solutions to exercises

E6.1(b) $2\,\text{A} \rightarrow \text{B}$

$n_{\text{J}} = n_{\text{J}}(0) + \nu_{\text{J}}\Delta\xi$, where ξ is the extent of reaction; ν_{J} is negative for reactants and positive for products.

$$n_{\text{A}} = 1.75\text{ mol} - 2 \times (0.30\text{ mol}) = \boxed{1.15\text{ mol}}$$

$$n_{\text{B}} = 0.12\text{ mol} + 1 \times (0.30\text{ mol}) = \boxed{0.42\text{ mol}}$$

E6.2(b) $2\,\text{A} \rightarrow \text{B} \quad \Delta_{\text{r}}G = -2.41\text{ kJ mol}^{-1}$

$$\Delta_{\text{r}}G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}\ [6.1]$$

With the approximation that $\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \approx \frac{\Delta G}{\Delta \xi}$, which is valid when $\Delta\xi$ is very small, we find that

$$\Delta G \approx \Delta_{\text{r}}G \times \Delta\xi \approx (-2.41\text{ kJ mol}^{-1}) \times (+0.051\text{ mol}) = \boxed{-0.12\text{ kJ}}$$

6.3(b) $2\,\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g}) \quad \Delta_{\text{r}}G^{\ominus} = -4.73\text{ kJ mol}^{-1}$

$$\Delta_{\text{r}}G = \Delta_{\text{r}}G^{\ominus} + RT\ln Q\,[6.10] = (-4.73\text{ kJ mol}^{-1}) + (2.4790\text{ kJ mol}^{-1}) \times \ln Q \quad \text{at } 298.15\text{ K}$$

Part	Q	$\Delta_{\text{r}}G/\text{kJ mol}^{-1}$
(a)	0.10	−10.44
(b)	1.0	−4.73
(c)	10	+0.98
(d)	100	+6.69

Figure 6.1 shows a plot of $\Delta_r G$ against Q. $K = Q_{\text{equilibrium}}$ when $\Delta_r G = 0$ so we find the equilibrium constant by interpolating the plot to the point at which $\Delta_r G = 0$ and read the value of Q at that point to find that $K \sim \boxed{7}$. Although the plot is very interesting and indicates a more exacting curvature, the estimate for the equilibrium constant can also be made with a linear interpolation between the points of parts (b) and (c). The graphical interpolation approximation agrees with the value calculated with eqn 6.14:

$$K = e^{-\Delta_r G^\ominus/RT} \; [6.14]$$
$$= e^{-(-4.73\,\text{kJ mol}^{-1})/(2.4790\,\text{kJ mol}^{-1})} = 6.74$$

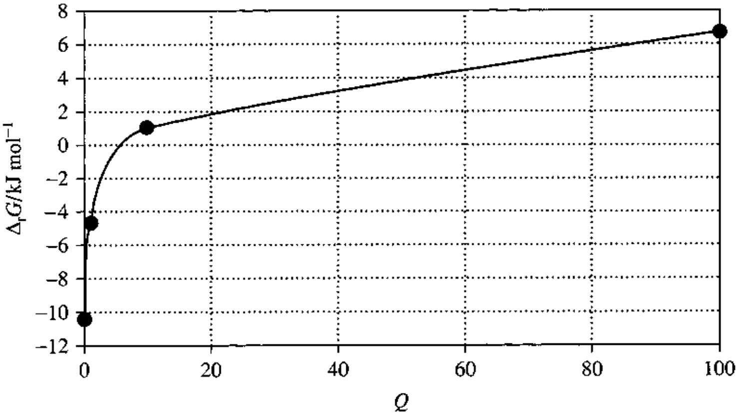


Figure 6.1

E6.4(b) $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ $\quad T = 298.15$ K, $p = 1$ bar $= p^\ominus$, $\alpha = 0.201$ at equilibrium.

We draw up the following equilibrium table (Example 6.2):

	$N_2O_4(g)$	$NO_2(g)$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)p}{1+\alpha}$	$\dfrac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6.13] = \left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}} \quad \text{[perfect gas assumption]}$$

$$= \frac{(p_{NO_2}/p^\ominus)^2}{p_{N_2O_4}/p^\ominus} = \frac{p_{NO_2}^2}{p_{N_2O_4}p^\ominus} = \frac{\left(\dfrac{2\alpha p}{1+\alpha}\right)^2}{\left(\dfrac{(1-\alpha)p}{1+\alpha}\right)p^\ominus}$$

$$= \frac{4p}{p^\ominus}\left\{\frac{\alpha^2}{(1-\alpha)\times(1+\alpha)}\right\} = 4\left\{\frac{(0.201)^2}{(1-0.201)\times(1+0.201)}\right\} = \boxed{0.168}$$

E6.5(b) (a) $Br_2(g) \rightleftharpoons 2\,Br(g)$ $T = 1600\ K, p = 1\ bar = p^\ominus, \alpha = 0.24$ at equilibrium.

We draw up the following equilibrium table (Example 6.2):

	$Br_2(g)$	$Br(g)$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)p}{1+\alpha}$	$\dfrac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6.13] = \left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}} \quad \text{[perfect gas assumption]}$$

$$= \frac{(p_{Br}/p^\ominus)^2}{p_{Br_2}/p^\ominus} = \frac{p_{Br}^2}{p_{Br_2}p^\ominus} = \frac{\left(\dfrac{2\alpha p}{1+\alpha}\right)^2}{\left(\dfrac{(1-\alpha)p}{1+\alpha}\right)p^\ominus}$$

$$= \frac{4p}{p^\ominus}\left\{\frac{\alpha^2}{(1-\alpha)\times(1+\alpha)}\right\} = 4\left\{\frac{(0.24)^2}{(1-0.24)\times(1+0.24)}\right\}$$

$$= \boxed{0.24\bar{4}} \text{ at } 1600\ K$$

(b) $\ln K_2 = \ln K_1 - \dfrac{\Delta_r H^\ominus}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6.23]

$$\ln K_{2000\,K} = \ln K_{1600\,K} - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{2000\ K} - \frac{1}{1600\ K}\right)$$

$$= \ln(0.24\bar{4}) - \left(\frac{+112\times10^3\ J\ mol^{-1}}{8.3145\ J\ K^{-1}\,mol^{-1}}\right)\times\left(\frac{1}{2000\ K} - \frac{1}{1600\ K}\right) = 027\bar{3}$$

$$K_{2000\,K} = e^{0.27\bar{3}} = \boxed{1.3}$$

As expected, the temperature increase causes a shift to the right when the reaction is endothermic.

.6(b) $CH_4(g) + 3\,Cl_2(g) \rightleftharpoons CHCl_3(l) + 3\,HCl(g)$

(a) Using data tables at 25°C, we find

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(CHCl_3,l) + 3\,\Delta_f G^\ominus(HCl,g) - \Delta_f G^\ominus(CH_4,g)\\ &= (-73.66\ KJ\ mol^{-1}) + (3)\times(-95.30\ KJ\ mol^{-1}) - (-50.72\ KJ\ mol^{-1})\\ &= \boxed{-308.84\ kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(CHCl_3,l) + 3\,\Delta_f H^\ominus(HCl,g) - \Delta_f H^\ominus(CH_4,g)\\ &= (-134.47\ kJ\ mol^{-1}) + (3)\times(-92.31\ kJ\ mol^{-1}) - (-74.81\ kJ\ mol^{-1})\\ &= -336.59\ kJ\ mol^{-1}\end{aligned}$$

$$\ln K = \frac{-\Delta_r G^\ominus}{RT}[6.14] = \frac{-(-308.84\times 10^3\text{ J mol}^{-1})}{(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(298.15\text{ K})} = 124.6$$

$$K = e^{124.6} = \boxed{1.30\times 10^{54}}$$

(b) $$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)[6.23]$$

$$\ln K_{50°\text{C}} = \ln K_{25°\text{C}} - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323.15\text{ K}}-\frac{1}{298.15\text{ K}}\right)$$

$$= \ln(1.30\times 10^{54}) - \left(\frac{-336.59\times 10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{mol}^{-1}}\right)\times\left(\frac{1}{323.15\text{ K}}-\frac{1}{298.15\text{ K}}\right) = 114.\bar{1}$$

$$K_{50°\text{C}} = e^{114.\bar{1}} = \boxed{3.57\times 10^{49}}$$

As expected, the temperature increase causes a shift to the left when the reaction is exothermic.

$$\Delta_r G^\ominus = -RT\ln K[6.14]$$

$$\Delta_r G^\ominus_{50°\text{C}} = -(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(323.15\text{ K})\ln(3.75\times 10^{49}) = \boxed{-307\text{ kJ mol}^{-1}}$$

E6.7(b) $3\,N_2(g) + H_2(g) \rightarrow 2\,HN_3(g)$ For this gas phase reaction $\Delta\nu = \sum_J \nu_J = -2$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6.13] = \left(\prod_J (\gamma_J p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= \left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= K_\gamma K_p,\quad \text{where}\quad K_\gamma = \left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\quad\text{and}\quad K_p = \left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma = 1$. Additionally, $p_J = n_J RT/V = [J]RT$. Substitution gives

$$K = K_p = \left(\prod_J ([J]RT/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J ([J]/c^\ominus)^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J (c^\ominus RT/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= K_c(c^\ominus RT/p^\ominus)^{\Delta\nu},\quad \text{where}\quad K_c = \left(\prod_J ([J]/c^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$K = K_c\times(c^\ominus RT/p^\ominus)^{-2}$ because $\Delta\nu = -2$ for this reaction

Since $c^\ominus R/p^\ominus = 0.0831451\text{ K}^{-1}$, this expression may be written in the form

$$\boxed{K = (144.653\text{ K}^2)\times K_c/T^2}$$

Anhydrous hydrogen azide, HN_3, boils at 36°C and decomposes explosively. A dilute solution can be handled safely.

E6.8(b) Draw up the following table for the reaction equation $A + B \rightleftharpoons C + 2\,D$:

	A	B	C	D	Total
Initial amounts/mol	2.00	1.00	0	3.00	6.00
Stated change/mol			+0.79		
Implied change/mol	−0.79	−0.79	+0.79	+1.58	
Equilibrium amounts/mol	1.21	0.21	0.79	4.58	6.79
Mole fractions	$0.178\overline{2}$	$0.030\overline{9}$	$0.116\overline{3}$	$0.674\overline{5}$	$0.999\overline{9}$

(a) Mole fractions are given in the table.

(b) $K_x = \prod_J x_J^{\nu_J}$

$$K_x = \frac{(0.116\overline{3}) \times (0.674\overline{5})^2}{(0.178\overline{2}) \times (0.030\overline{9})} = \boxed{9.61}$$

(c) $p_J = x_J p$. Assuming the gases are perfect, $a_J = p_J/p^{\ominus}$, so

$$K = \frac{(p_C/p^{\ominus}) \times (p_D/p^{\ominus})^2}{(p_A/p^{\ominus}) \times (p_B/p^{\ominus})} = K_x\left(\frac{p}{p^{\ominus}}\right) = K_x, \quad \text{when } p = 1.00 \text{ bar}$$

$$K = K_x = \boxed{9.61}$$

(d) $\Delta_r G^{\ominus} = -RT \ln K = -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K}) \times \ln(9.61) = \boxed{-5.61\ \mathrm{kJ\ mol^{-1}}}$

E6.9(b) At 1120 K, $\Delta_r G^{\ominus} = +22 \times 10^3\ \mathrm{J\ mol^{-1}}$

$$\ln K_1(1120\ \mathrm{K}) = -\frac{\Delta_r G^{\ominus}}{RT} = -\frac{(22 \times 10^3\ \mathrm{J\ mol^{-1}})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (1120\ \mathrm{K})} = -2.3\overline{63}$$

$$K = \mathrm{e}^{-2.3\overline{63}} = 9.\overline{41} \times 10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solve for T_2 at $\ln K_2 = 0$ ($K_2 = 1$)

$$\frac{1}{T_2} = \frac{R \ln K_1}{\Delta_r H^{\ominus}} + \frac{1}{T_1} = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (-2.3\overline{63})}{(125 \times 10^3\ \mathrm{J\ mol^{-1}})} + \frac{1}{1120\ \mathrm{K}} = 7.3\overline{6} \times 10^{-4}$$

$$T_2 = \boxed{1.4 \times 10^3\ \mathrm{K}}$$

.10(b) $\ln K = A + \dfrac{B}{T} + \dfrac{C}{T^3}$, where $A = -2.04$, $B = -1176$ K, and $C = 2.1 \times 10^7\ \mathrm{K^3}$

At 450 K:

$$\Delta_r G^{\ominus} = -RT \ln K\,[6.14] = RT \times \left(A + \frac{B}{T} + \frac{C}{T^3}\right)$$

$$= -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (450\ \mathrm{K}) \times \left(-2.04 - \frac{1176\ \mathrm{K}}{450\ \mathrm{K}} + \frac{2.1 \times 10^7\ \mathrm{K^3}}{(450\ \mathrm{K})^3}\right) = +16.6\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r H^\ominus = -R\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)}\ [6.21(\mathrm{b})]$$

$$= -R\frac{\mathrm{d}}{\mathrm{d}(1/T)}\left(A+\frac{B}{T}+\frac{C}{T^3}\right) = -R\times\left(B+\frac{3C}{T^2}\right)$$

$$= -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times\left\{(-1176\ \mathrm{K})+3\times\frac{2.1\times10^7\ \mathrm{K}^3}{(450\ \mathrm{K})^2}\right\}$$

$$= \boxed{+7.19\ \mathrm{kJ\ mol^{-1}}}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{7.19\ \mathrm{kJ\ mol^{-1}} - 16.6\ \mathrm{kJ\ mol^{-1}}}{450\ \mathrm{K}} = \boxed{-20.9\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

E6.11(b) $3\,N_2(g) + H_2(g) \rightarrow 2\,HN_3(g)$. For this gas-phase reaction $\Delta\nu = \sum_J \nu_J = -2$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6.13] = \left(\prod_J (\gamma_J p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= K_\gamma K_p, \quad \text{where} \quad K_\gamma = \left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}} \quad \text{and } K_p = \left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma = 1$. Additionally, $p_J = n_J RT/V = [J]RT$. Substitution gives

$$K = K_p = \left(\prod_J ([J]RT/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J ([J]/c^\ominus)^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J (c^\ominus RT/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= K_c (c^\ominus RT/p^\ominus)^{\Delta\nu}, \quad \text{where} \quad K_c = \left(\prod_J ([J]/c^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$K = K_c \times (c^\ominus RT/p^\ominus)^{-2}$ because $\Delta\nu = -2$ for this reaction.

Since $c^\ominus R/p^\ominus = 0.0831451\ \mathrm{K^{-1}}$, this expression may be written in the form

$$\boxed{K = (144.653\ \mathrm{K}^2)\times K_c/T^2}$$

Anhydrous hydrogen azide, HN_3, boils at 36°C and decomposes explosively. A dilute solution can be handled safely.

E6.12(b) $3\,N_2(g) + H_2(g) \rightarrow 2\,HN_3(g)$. For this gas-phase reaction $\Delta\nu = \sum_J \nu_J = -2$

$$\Delta_r H^\ominus = \Delta_f H^\ominus(HN_3,g) = +294.1\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus(HN_3,g) = +328.1\ \mathrm{kJ\ mol^{-1}}$$

Also, from Exercise 6.11(b) we have the relationship

$$K_c = K\times T^2/(144.653\ \mathrm{K}^2)$$

(a) At 25°C

$$K_{25°\mathrm{C}} = \mathrm{e}^{-\Delta_r G^\ominus/RT}\,[6.14]$$

$$= \mathrm{e}^{-(+328.1\ \mathrm{kJ\ mol^{-1}})/(2.4790\ \mathrm{kJ\ mol^{-1}})} = \boxed{3.308 \times 10^{-58}}$$

$$K_c(25°\mathrm{C}) = K_{25°\mathrm{C}} \times T^2/(144.653\ \mathrm{K}^2)\}$$

$$= (3.308 \times 10^{-58}) \times (298.15\ \mathrm{K})^2/(144.653\ \mathrm{K}^2) = \boxed{2.033 \times 10^{-55}}$$

(b) At 100°C

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\,[6.23]$$

$$\ln K_{100°\mathrm{C}} = \ln K_{25°\mathrm{C}} - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{373.15\ \mathrm{K}} - \frac{1}{298.15\ \mathrm{K}}\right)$$

$$= \ln(3.308 \times 10^{-58}) - \left(\frac{+294.1 \times 10^3\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\right) \times \left(\frac{1}{373.15\ \mathrm{K}} - \frac{1}{298.15\ \mathrm{K}}\right)$$

$$= -108.5$$

$$K_{100°\mathrm{C}} = \mathrm{e}^{-108.5} = \boxed{7.569 \times 10^{-48}}$$

$$K_c(100°\mathrm{C}) = K_{100°\mathrm{C}} \times T^2/(144.653\ \mathrm{K}^2)$$

$$= (7.569 \times 10^{-48}) \times (373.15\ \mathrm{K})^2/(144.653\ \mathrm{K}^2) = \boxed{7.286 \times 10^{-45}}$$

The extremely small equilibrium constants tell us that hydrogen azide is not to be prepared directly from the elements. It is interesting to contrast the calculations with those for the formation of ammonia. The balanced reaction equation, $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$, also gives $\Delta\nu = \sum_J \nu_J = -2$ so the relationship of Exercise 6.11(b) is identically applicable: $K_c = K \times T^2/(144.653\ \mathrm{K}^2)$. The calculations are identical to those above and we find the following results:

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\mathrm{NH_3,g}) = -46.11\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\mathrm{NH_3,g}) = -16.45\ \mathrm{kJ\ mol^{-1}}$$

$$K_{25°\mathrm{C}} = \mathrm{e}^{-\Delta_r G^\ominus/RT}\ [6.14] = \mathrm{e}^{-(-16.45\ \mathrm{kJ\ mol^{-1}})/(2.4790\ \mathrm{kJ\ mol^{-1}})} = 762$$

$$K_c(25°\mathrm{C}) = K_{25°\mathrm{C}} \times T^2/(144.653\ \mathrm{K}^2) = (762) \times (298.15\ \mathrm{K})^2/(144.653\ \mathrm{K}^2) = 4.68 \times 10^5$$

$$\ln K_{100°\mathrm{C}} = \ln K_{25°\mathrm{C}} - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{373.15\ \mathrm{K}} - \frac{1}{298.15\ \mathrm{K}}\right)$$

$$= \ln(762) - \left(\frac{-46.11 \times 10^3\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\right) \times \left(\frac{1}{373.15\ \mathrm{K}} - \frac{1}{298.15\ \mathrm{K}}\right) = 6.63\overline{2}$$

$$K_{100°\mathrm{C}} = \mathrm{e}^{6.63\overline{2}} = 759$$

$$K_c(100°\mathrm{C}) = K_{100°\mathrm{C}} \times T^2/(144.653\ \mathrm{K}^2) = (759) \times (373.15\ \mathrm{K})^2/(144.653\ \mathrm{K}^2) = 7.31 \times 10^5$$

The equilibrium constants for ammonia formation are large, which makes ammonia production from the elements feasible. There are, however, kinetic difficulties with the direct production that are resolved in the Haber process by using elevated temperature and pressure along with a catalyst.

E6.13(b) The formation reaction is $U(s)+\frac{3}{2}H_2(g) \rightleftharpoons UH_3(s)$.

$$K=\frac{1}{a^{3/2}_{H_2(g)}}=\left(\frac{p^\ominus}{p_{H_2}}\right)^{3/2} \quad [a_{U(s)}=a_{UH_3(s)}=1 \text{ and, assuming perfect gas behaviour, } a_{H_2(g)}=p_{H_2}/p^\ominus.]$$

$$=\left(\frac{10^5\ \text{Pa}}{139\ \text{Pa}}\right)^{3/2}=1.93\times10^4$$

$$\Delta_r G^\ominus=-RT\ln K\,[6.14]$$
$$=-(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(500\ \text{K})\times\ln(1.93\times10^4)$$
$$=\boxed{-41.0\ \text{kJ mol}^{-1}}$$

E6.14(b) $CH_3OH(g)+NOCl(g)\rightarrow HCl(g)+CH_3NO_2(g)$. For this gas-phase reaction $\Delta\nu=\sum_J \nu_J=0$

$$K=\left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}}[6.13]=\left(\prod_J(\gamma_J p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}=\left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$=K_\gamma K_p, \quad \text{where} \quad K_\gamma=\left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}} \quad \text{and} \quad K_p=\left(\prod_J (p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma=1$. Additionally, $p_J=x_J p$. Substitution gives

$$K=K_p=\left(\prod_J (x_J p/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}=\left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J (p/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$=K_x(p/p^\ominus)^{\Delta\nu}, \quad \text{where} \quad K_x=\left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}}$$

For this reaction: $K=K_x\times(p/p^\ominus)^0=K_x$ because $\Delta\nu=0$

K is independent of pressure so we conclude by the above eqn that for this reaction K_x is also independent of pressure. Thus, the percentage change in K_x on changing the pressure equals $\boxed{\text{zero}}$ for this reaction.

E6.15(b) $N_2(g)+O_2(g)\rightleftharpoons 2\,NO(g)$ $K=1.69\times10^{-3}$ at 2300 K

Initial modes: $n_{N_2}=\dfrac{5.0\ \text{g}}{28.013\ \text{g mol}^{-1}}=0.1\overline{785}\ \text{mol}$

Initial moles: $n_{O_2}=\dfrac{2.0\ \text{g}}{32.00\ \text{g mol}^{-1}}=6.2\overline{50}\times10^{-2}\ \text{mol}$

	N_2	O_2	NO	Total
Initial amount/mol	$n_{N_2} = 0.17\overline{85}$	$n_{O_2} = 0.062\overline{5}$	0	$n = 0.2410$
Change/mol	$-z$	$-z$	$+2z$	0
Equilibrium amount/mol	$n_{N_2} - z$	$n_{O_2} - z$	$2z$	$n = 0.2410$
Mole fractions	$(n_{N_2} - z)/n$	$(n_{O_2} - z)/n$	$2z/n$	1

$$K = K_x\left(\frac{p}{p^{\ominus}}\right)^{\Delta\nu} = K_x \text{ [because } \Delta\nu = \sum_J \nu_J = 0 \text{ for this reaction]}$$

$$K = \frac{(2z)^2}{(n_{N_2} - z) \times (n_{O_2} - z)}$$

$$\left(1 - \tfrac{4}{K}\right)z^2 - nz + n_{N_2}n_{O_2} = 0$$

$$z = \frac{n \pm \sqrt{n^2 - 4\left(1 - \tfrac{4}{K}\right)n_{N_2}n_{O_2}}}{2\left(1 - \tfrac{4}{K}\right)}$$

$$= \frac{0.2410 \pm \sqrt{0.2410^2 - 4\left(1 - \frac{4}{1.69\times10^{-3}}\right)(0.1785)(0.0625)}}{2\left(1 - \frac{4}{1.69\times10^{-3}}\right)}$$

$$= -2.223 \times 10^{-3} \quad \text{or} \quad 2.121 \times 10^{-3}$$

$$= 2.121 \times 10^{-3} \quad \text{because the negative value is non-physical}$$

$$x_{NO} = \frac{2z}{n} = \frac{2(2.121 \times 10^{-3})}{0.24\overline{1}} = \boxed{1.8 \times 10^{-2}}$$

E6.16(b)

$$\ln\frac{K_2}{K_1} = -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ [6.23]}$$

$$\Delta_r H^{\ominus} = R \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \times \ln\left(\frac{K_2}{K_1}\right)$$

$$= (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times \left(\frac{1}{310 \text{ K}} - \frac{1}{325 \text{ K}}\right)^{-1} \times \ln\left(\frac{K_2}{K_1}\right)$$

$$= (55.85 \text{ kJ mol}^{-1}) \times \ln\left(\frac{K_2}{K_1}\right)$$

(a) $K_2/K_1 = 2.00$

$$\Delta_r H^{\ominus} = (55.85 \text{ kJ mol}^{-1}) \times \ln(2.00) = \boxed{38.71 \text{ kJ mol}^{-1}}$$

(b) $K_2/K_1 = 0.500$

$$\Delta_r H^{\ominus} = (55.85 \text{ kJ mol}^{-1}) \times \ln(0.500) = \boxed{-38.71 \text{ kJ mol}^{-1}}$$

E6.17(b) $\mathrm{NH_4Cl(s)} \rightleftharpoons \mathrm{NH_3(g)} + \mathrm{HCl(g)}$

Vapour pressures: $p_{427°\mathrm{C}} = 608\ \mathrm{kPa}$ and $p_{459°\mathrm{C}} = 1115\ \mathrm{kPa}$.

The gases originate from the dissociation of the solid alone so $p_{\mathrm{NH_3}} = p_{\mathrm{HCl}} = \frac{1}{2}p$.

(a) Equilibrium constants

$$K = (p_{\mathrm{NH_3}}/p^{\ominus}) \times (p_{\mathrm{HCl}}/p^{\ominus}) \quad \text{[perfect gas assumption]}$$

$$= \left(\tfrac{1}{2}p/p^{\ominus}\right) \times \left(\tfrac{1}{2}p/p^{\ominus}\right)$$

$$= \tfrac{1}{4}(p/p^{\ominus})^2$$

$$K_{427°\mathrm{C}} = \tfrac{1}{4}(608\ \mathrm{kPa}/100\ \mathrm{kPa})^2 = \boxed{9.24}$$

$$K_{459°\mathrm{C}} = \tfrac{1}{4}(1115\ \mathrm{kPa}/100\ \mathrm{kPa})^2 = 31.08$$

(b) $\Delta_r G^{\ominus} = -RT\ln K\,[6.14]$

$$\Delta_r G^{\ominus}_{427°\mathrm{C}} = -(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (700.15\ \mathrm{K}) \times \ln(9.24) = \boxed{-12.9\ \mathrm{kJ\,mol^{-1}}}$$

(c) $\ln\dfrac{K_2}{K_1} = -\dfrac{\Delta_r H^{\ominus}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6.23]

$$\Delta_r H^{\ominus} = R \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \times \ln\left(\frac{K_2}{K_1}\right)$$

$$= (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\frac{1}{700.15\ \mathrm{K}} - \frac{1}{732.15\ \mathrm{K}}\right)^{-1} \times \ln\left(\frac{31.08}{9.24}\right)$$

$$= \boxed{162\ \mathrm{kJ\,mol^{-1}}}$$

(d) $\Delta_r S^{\ominus} = \dfrac{\Delta_r H^{\ominus} - \Delta_r G^{\ominus}}{T} = \dfrac{(162\ \mathrm{kJ\,mol^{-1}}) - (-12.9\ \mathrm{kJ\,mol^{-1}})}{700.15\ \mathrm{K}} = \boxed{+250\ \mathrm{J\,K^{-1}\,mol^{-1}}}$

E6.18(b) The reaction is $\mathrm{CuSO_4 \cdot 5\,H_2O(s)} \rightleftharpoons \mathrm{CuSO_4(s)} + 5\,\mathrm{H_2O(g)}$.

For the purposes of this exercise we may assume that the required temperature is that temperature at which $K = 1$, which corresponds to a pressure of 1 bar for the gaseous products. For $K = 1$, $\ln K = 0$, and $\Delta_r G^{\ominus} = 0$.

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} = 0 \quad \text{when } \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

Therefore, the decomposition temperature (when $K = 1$) is

$$T = \frac{\Delta_r H^{\ominus}}{\Delta_r S^{\ominus}}$$

$$\Delta_r H^{\ominus} = \sum_J \nu_J \Delta_{f,J} H^{\ominus} = \{(-771.36) + (5) \times (-241.82) - (-2279.7)\}\ \mathrm{J\,mol^{-1}} = +299.2\ \mathrm{kJ\,mol^{-1}}$$

$$\Delta_r S^{\ominus} = \sum_J \nu_J S_J^{\ominus} = \{(109) + (5) \times (188.83) - (300.4)\}\ \mathrm{J\,K^{-1}\,mol^{-1}} = 752.\bar{8}\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Therefore, $T = \dfrac{299.2 \times 10^3\,\text{J mol}^{-1}}{752.8\,\text{J K}^{-1}\,\text{mol}^{-1}} = \boxed{397\,\text{K}}$

Question. What would the decomposition temperature be for decomposition defined as the state at which $K = \frac{1}{2}$?

E6.19(b) $\text{PbI}_2(\text{s}) \rightleftharpoons \text{PbI}_2(\text{aq}) \quad K_s = 1.4 \times 10^{-8}$

$$\begin{aligned}\Delta_r G^\ominus &= -RT \ln K_s \\ &= -(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K}) \times \ln(1.4 \times 10^{-8}) = +44.8\,\text{kJ mol}^{-1} \\ &= \Delta_f G^\ominus(\text{PbI}_2,\text{aq}) - \Delta_f G^\ominus(\text{PbI}_2,\text{s})\end{aligned}$$

$$\begin{aligned}\Delta_f G^\ominus(\text{PbI}_2,\text{aq}) &= \Delta_r G^\ominus + \Delta_f G^\ominus(\text{PbI}_2,\text{s}) \\ &= (44.8 - 173.64)\,\text{kJ mol}^{-1} = \boxed{-128.8\,\text{kJ mol}^{-1}}\end{aligned}$$

E6.20(b) The cell notation specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined. For the calculation of the standard cell potentials we have used $E^\ominus_{\text{cell}} = E^\ominus_{\text{R}} - E^\ominus_{\text{L}}$, with standard electrode potentials from data tables.

		$E^\ominus$
(a)	R: $\text{Ag}_2\text{CrO}_4(\text{s}) + 2\,\text{e}^- \rightarrow 2\,\text{Ag(s)} + \text{CrO}_4^{2-}(\text{aq})$	+0.45 V
	L: $\text{Cl}_2(\text{g}) + 2\,\text{e}^- \rightarrow 2\,\text{Cl}^-(\text{aq})$	+1.36 V
	Overall (R – L): $\text{Ag}_2\text{CrO}_4(\text{s}) + 2\,\text{Cl}^-(\text{aq}) \rightarrow 2\,\text{Ag(s)} + \text{CrO}_4^{2-}(\text{aq}) + \text{Cl}_2(\text{g})$	–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: $\text{MnO}_2(\text{s}) + 4\,\text{H}^+(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\,\text{H}_2\text{O(l)}$	+1.23 V
	L: $\text{Cu}^{2+}(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Cu(s)}$	+0.34 V
	Overall (R – L): $\text{Cu(s)} + \text{MnO}_2(\text{s}) + 4\,\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 2\,\text{H}_2\text{O(l)}$	+0.89 V

COMMENT. Those cells for which $E^\ominus_{\text{cell}} > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E^\ominus_{\text{cell}} < 0$ may operate as nonspontaneous electrolytic cells. Recall that $E^\ominus_{\text{cell}}$ informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E_{cell}.

6.21(b) The conditions (concentrations, etc.) under which these reactions occur are not given. For the purposes of this exercise we assume standard conditions. The specification of the right and left electrodes is determined by the direction of the reaction as written. As always, in combining half-reactions to form an overall cell reaction we must write half-reactions with equal numbers of electrons to ensure proper cancellation. We first identify the half-reactions and then set up the corresponding cell.

		$E^\ominus$
(a)	R: $2\,\text{H}_2\text{O(l)} + 2\,\text{e}^- \rightarrow 2\,\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$	–0.83 V
	L: $2\,\text{Na}^+(\text{aq}) + 2\,\text{e}^- \rightarrow 2\,\text{Na(s)}$	–2.71 V
	and the cell is	
	$\text{Na(s)}\,|\,\text{NaOH(aq)}\,|\,\text{H}_2(\text{g})\,|\,\text{Pt}$	$\boxed{+1.88\,\text{V}}$

(b) R: $I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$ $+0.54$ V

L: $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ 0

and the cell is

$Pt|H_2(g)|H^+(aq), I^-(aq)|I_2(s)|Pt$ $\boxed{+0.54\ \text{V}}$

(c) R: $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ 0

L: $2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$ -0.83

and the cell is

$Pt|H_2(g)|OH^-(aq)||H^+(aq)|H_2(g)|Pt$ $\boxed{+0.83\ \text{V}}$

COMMENT. All of these cells have $E^\ominus_{\text{cell}} > 0$, corresponding to a spontaneous cell reaction under standard conditions. If $E^\ominus_{\text{cell}}$ had turned out to be negative, the spontaneous reaction would have been the reverse of the one given, with the right and left electrodes of the cell also reversed.

E6.22(b) $Pt|H_2(g,p^\ominus)|HCl(aq, 0.010\ \text{mol kg}^{-1})|AgCl(s)|Ag(s)$

(a) R: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ $E^\ominus = +0.22$ V

L: $HCl(aq) + e^- \rightarrow \tfrac{1}{2}\,H_2(g) + Cl^-(aq)$ $E^\ominus = +0.00$ V

$2 \times R - 2 \times L$: $2\,AgCl(s) + H_2(g) \rightarrow 2\,Ag(s) + 2\,HCl(aq)$ $E^\ominus_{\text{cell}} = +0.22$ V and $\nu = 2$

The cell reaction is spontaneous toward the right under standard conditions because $E^\ominus_{\text{cell}} > 0$. The Nernst equation for the above cell reaction is:

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{\nu F}\ln Q\ [6.27]$$

$$Q = \frac{(a_{\text{HCl(aq)}})^2}{a_{\text{H}_2\text{(g)}}} = \frac{(a_{\text{H}^+\text{(aq)}}a_{\text{Cl}^-\text{(aq)}})^2}{a_{\text{H}_2\text{(g)}}} = \frac{(\gamma_\pm^2(b_{\text{HCl}}/b^\ominus)^2)^2}{p/p^\ominus} = \gamma_\pm^4(b_{\text{HCl}}/b^\ominus)^4\ \text{(i.e. } p = p^\ominus)$$

Thus,

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{2F}\ln\{\gamma_\pm^4(b_{\text{HCl}}/b^\ominus)^4\} \quad \text{or} \quad \boxed{E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{2RT}{F}\ln\{\gamma_\pm(b_{\text{HCl}}/b^\ominus)\}}$$

(b) $\Delta_r G^\ominus = -\nu F E^\ominus_{\text{cell}} = -2 \times (9.6485 \times 10^4\ \text{C mol}^{-1}) \times (0.22\ \text{V}) = \boxed{-42\ \text{kJ mol}^{-1}}$

(c) The ionic strength and mean activity coefficient are:

$$I = \tfrac{1}{2}\sum_i z_i^2(b_i/b^\ominus)\ [5.76] = \tfrac{1}{2}\{1(0.010) + 1(.010)\} = 0.010$$

$$\log \gamma_\pm = -|z_+z_-|AI^{1/2}\ [5.75] = -1 \times (0.509) \times (0.010)^{1/2} = -0.0509$$

$$\gamma_\pm = 0.889$$

Therefore,

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{2RT}{F}\ln\{\gamma_\pm(b_{\text{HCl}}/b^\ominus)\}$$

$$= 0.22\ \text{V} - \frac{2 \times (8.3145\ \text{J mol}^{-1}\,\text{K}^{-1}) \times (298.15\ \text{K})}{9.6485 \times 10^5\,\text{C mol}^{-1}}\ln\{(0.889) \times (0.010)\} = 0.22\ \text{V} + 0.24\ \text{V}$$

$$= \boxed{+0.46\ \text{V}}$$

E6.23(b) In each case the equilibrium constant is calculated by the expression $\ln K = \dfrac{\nu F E^{\ominus}_{\text{cell}}}{RT}$ [6.28].

(a) $\text{Sn(s)} + \text{CuSO}_4\text{(aq)} \rightleftharpoons \text{Cu(s)} + \text{SnSO}_4\text{(aq)}$

$$\left.\begin{aligned} &\text{R: Cu}^{2+} + 2\,\text{e}^- \rightarrow \text{Cu(s)} && +0.34\ \text{V} \\ &\text{L: Sn}^{2+}\text{(aq)} + 2\,\text{e}^- \rightarrow \text{Sn(s)} && -0.14\ \text{V} \end{aligned}\right\} E^{\ominus}_{\text{cell}} = +0.48\ \text{V}$$

$$\ln K = \frac{\nu F E^{\ominus}_{\text{cell}}}{RT}\ [6.28] = \frac{(2) \times (0.48\ \text{V})}{25.693\ \text{mV}} = 37.\overline{4}$$

$$K = \text{e}^{37.\overline{4}} = \boxed{1.7 \times 10^{16}}$$

(b) $\text{Cu(s)} + \text{Cu}^{2+}\text{(aq)} \rightleftharpoons 2\,\text{Cu}^+\text{(aq)}$

$$\left.\begin{aligned} &\text{R: Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+\text{(aq)} && +0.16\ \text{V} \\ &\text{L: Cu}^+\text{(aq)} + \text{e}^- \rightarrow \text{Cu(s)} && +0.52\ \text{V} \end{aligned}\right\} E^{\ominus}_{\text{cell}} = -0.36\ \text{V}$$

$$\ln K = \frac{\nu F E^{\ominus}_{\text{cell}}}{RT}\ [6.28] = \frac{(1) \times (-0.36\ \text{V})}{25.693\ \text{mV}} = -14.\overline{0}$$

$$K = \text{e}^{-14.\overline{0}} = \boxed{8.3 \times 10^{-7}}$$

24(b) R: $2\,\text{Bi}^{3+}\text{(aq)} + 6\,\text{e}^- \rightarrow 2\,\text{Bi(s)}$
L: $\text{Bi}_2\text{S}_3\text{(s)} + 6\,\text{e}^- \rightarrow 2\,\text{Bi(s)} + 3\,\text{S}^{2-}\text{(aq)}$
Overall (R − L): $2\,\text{Bi}^{3+}\text{(aq)} + 3\,\text{S}^{2-}\text{(aq)} \rightarrow \text{Bi}_2\text{S}_3\text{(s)}$ and $\nu = 6$, $E^{\ominus}_{\text{cell}} = +0.96\ \text{V}$

(a) $\ln K = \dfrac{\nu F E^{\ominus}_{\text{cell}}}{RT}\ [6.28] = \dfrac{6(0.96\ \text{V})}{(25.693 \times 10^{-3}\ \text{V})} = 22\overline{4}$

$$K = \text{e}^{22\overline{4}} = 1.9 \times 10^{97}$$

The solubility equilibrium is written as the reverse of the cell reaction, therefore the solubility product of $\text{Bi}_2\text{S}_3\text{(s)}$ is $K_{\text{sp}} = K^{-1} = 1/1.9 \times 10^{97} = \boxed{5.3 \times 10^{-98}}$.

(b) The solubility product of $\text{Bi}_2\text{S}_3\text{(s)}$ is very small. Consequently, the molar solubility, s, of $\text{Bi}_2\text{S}_3\text{(s)}$ must also be very low and we can reasonably take the activity coefficients of the aqueous ions to equal 1.

$$K_{\text{sp}} = [\text{Bi}^{2+}]^2[\text{S}^{2-}]^3/(c^{\ominus})^5 = (2s)^2(3s)^3/(c^{\ominus})^5 = 108(s/c^{\ominus})^5$$
$$s = (K_{\text{sp}}/108)^{1/5}c^{\ominus} = (5.3 \times 10^{-98}/108)^{1/5}\ \text{mol dm}^{-3} = \boxed{1.4 \times 10^{-20}\ \text{mol dm}^{-3}\ \text{or}\ 7.2\ \text{ag dm}^{-3}}$$

Solutions to problems

Solutions to numerical problems

6.2 $\text{CH}_4\text{(g)} \rightleftharpoons \text{C(s)} + 2\,\text{H}_2\text{(g)}$

This reaction is the reverse of the formation reaction. Consequently,

$$\begin{aligned} \Delta_r G^{\ominus} &= -\Delta_f G^{\ominus} = -(\Delta_f H^{\ominus} - T\Delta_f S^{\ominus}) \\ &= -\{-74.85\ \text{kJ mol}^{-1} - (298\ \text{K}) \times (-80.67\ \text{J K}^{-1}\ \text{mol}^{-1})\} \\ &= +50.81\ \text{kJ mol}^{-1} \end{aligned}$$

(a) $K = e^{-\Delta_r G^\ominus/RT}$ [6.14]

$$= e^{-(5.081\times10^4\,\mathrm{J\,mol^{-1}})/(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times298\,\mathrm{K})}$$

$$= \boxed{1.24\times10^{-9}}$$

(b) $\Delta_r H^\ominus = -\Delta_f H^\ominus = 74.85\ \mathrm{kJ\,mol^{-1}}$

$$\ln K(50°\mathrm{C}) = \ln K(298\ \mathrm{K}) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right)[6.23]$$

$$= -20.508 - \left(\frac{7.4850\times10^4\ \mathrm{J\,mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}\right)\times(-2.59\bar{7}\times10^{-4}) = -18.17\bar{0}$$

$$K(50°\mathrm{C}) = \boxed{1.29\times10^{-8}}$$

(c) Draw up the equilibrium table.

	$CH_4(g)$	$H_2(g)$
Amounts	$(1-\alpha)n$	$2\alpha n$
More fractions	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$
Partial pressures	$\left(\frac{1-\alpha}{1+\alpha}\right)p$	$\left(\frac{2\alpha}{1+\alpha}\right)p$

$$K = \prod_j a_j^{\nu_j}\ [6.13] = \frac{(p_{H_2}/p^\ominus)^2}{p_{CH_4}/p^\ominus} = \frac{\left(\left(\frac{2\alpha}{(1+\alpha)}\right)\frac{p}{p^\ominus}\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)\frac{p}{p^\ominus}}$$

$$= \frac{4\alpha^2 p/p^\ominus}{1-\alpha^2} \approx 4\alpha^2 p/p^\ominus\ [\text{since } K \ll 1, \text{ we expect } \alpha \ll 1]$$

$$\alpha = \left(\frac{K}{4p/p^\ominus}\right)^{1/2}$$

$$= \left(\frac{1.24\times10^{-9}}{4\times(0.010)}\right)^{1/2} = \boxed{1.8\times10^{-4}}$$

(d) Le Chatelier's principle provides the answers. As pressure increases, α decreases, since the more compact state (less moles of gas) is favoured at high pressures. As temperature increases the side of the reaction that can absorb heat is favoured. Since $\Delta_r H^\ominus$ is positive, that is the right-hand side, hence α increases. This can also be seen from the results of parts (a) and (b), K increased from 25 to 50°C, implying that α increased.

P6.4 $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$

Draw up the following equilibrium table and recognize that, since $\alpha \ll 1$, α may be neglected when compared to 1 within mole fraction factors.

	CO_2	CO	O_2
Amounts	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
Mole fractions	$\frac{1-\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$
Approximate mole fractions	1	α	$\frac{1}{2}\alpha$

$$K=\prod_J a_J^{\nu_J}\,[6.13]=\frac{(p_{CO}/p^\ominus)(p_{O_2}/p^\ominus)^{1/2}}{p_{CO_2}/p^\ominus}\text{ [perfect gases]}$$

$$=\frac{x_{CO}x_{O_2}^{1/2}}{x_{CO_2}}(p/p^\ominus)^{1/2}[p_J=x_Jp]$$

$$=\frac{x_{CO}x_{O_2}^{1/2}}{x_{CO_2}}[p=p^\ominus]$$

$$\approx\alpha\left(\tfrac{1}{2}\alpha\right)^{1/2}$$

$$\approx\left(\tfrac{1}{2}\alpha^3\right)^{1/2}\qquad\text{(i)}$$

$$\Delta_rG^\ominus=-RT\ln K\,[6.14]\qquad\text{(ii)}$$

The calculated values of K and $\Delta_rG^\ominus$ are given in the table below. From any two pairs of K and T, $\Delta_rH^\ominus$ may be calculated.

$$\ln K_2=\ln K_1-\frac{\Delta_rH^\ominus}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)[6.23]$$

Solving for $\Delta_rH^\ominus$:

$$\Delta_rH^\ominus=\frac{R\ln\left(\frac{K_2}{K_1}\right)}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}=\frac{(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times\ln\left(\frac{7.23\times10^{-6}}{1.22\times10^{-6}}\right)}{\left(\frac{1}{1395\text{ K}}-\frac{1}{1498\text{ K}}\right)}=\boxed{300\text{ kJ mol}^{-1}}$$

$$\Delta_rS^\ominus=\frac{\Delta_rH^\ominus-\Delta_rG^\ominus}{T}\qquad\text{(iii)}$$

K, $\Delta_rG^\ominus$, and $\Delta_rS^\ominus$ are calculated using equations (i), (ii), and (iii).

T/K	1395	1443	1498
$\alpha/10^{-4}$	1.44	2.50	4.71
$K/10^{-6}$	1.22	2.80	7.23
$\Delta_rG^\ominus$/kJ mol^{-1}	158	153	147
$\Delta_rS^\ominus$/J K^{-1} mol^{-1}	102	102	102

COMMENT. $\Delta_rS^\ominus$ is essentially constant over this temperature range but it is very different from its value at 25°C. $\Delta_rH^\ominus$, however, is only slightly different.

Question. What are the values of $\Delta_rH^\ominus$ and $\Delta_rS^\ominus$ at 25°C for this reaction?

P6.6 $\Delta_r G^\ominus(H_2CO,g) = \Delta_r G^\ominus(H_2CO,l) + \Delta_{vap}G^\ominus(H_2CO,l)$

For $H_2CO(l) \rightleftharpoons H_2CO(g)$, $K(\text{vap}) = \dfrac{p}{p^\ominus}$, where $p = 1500$ Torr $= 2.000$ bar and $p^\ominus = 1$ bar

$$\Delta_{vap}G^\ominus = -RT\ln K(\text{vap}) = RT\ln\frac{p}{p^\ominus}$$

$$= -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) \times \ln\left(\frac{2.000\ \text{bar}}{1\ \text{bar}}\right) = -1.72\ \text{kJ mol}^{-1}$$

Therefore, for the reaction $CO(g) + H_2(g) \rightleftharpoons H_2CO(g)$,

$$\Delta_r G^\ominus = \{(+28.95) + (-1.72)\}\ \text{kJ mol}^{-1} = +27.23\ \text{kJ mol}^{-1}$$

Hence, $K = e^{(-27.23\times10^3\ \text{J mol}^{-1})/(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})} = e^{-10.99} = \boxed{1.69\times10^{-5}}$.

P6.8 Draw up the following table for the reaction: $H_2(g) + I_2 \rightleftharpoons 2\,HI(g)$ $K = 870$.

	H_2	I_2	HI	Total
Initial amounts/mol	$n_{H_2} = 0.300$	$n_{I_2} = 0.400$	$n_{HI} = 0.200$	$n = 0.900$
Change/mol	$-z$	$-z$	$+2z$	
Equilibrium amount/mol	$n_{H_2} - z$	$n_{I_2} - z$	$n_{HI} + 2z$	$n = 0.900$
Mole fraction	$(n_{H_2} - z)/n$	$(n_{I_2} - z)/n$	$(n_{HI} + 2z)/n$	1

$$K = \frac{(p_{HI}/p^\ominus)^2}{(p_{H_2}/p^\ominus)(p_{I_2}/p^\ominus)}\ [\text{perfect gases, } p_J = x_J p]$$

$$= \frac{(x_{HI})^2}{(x_{H_2})(x_{I_2})} = \frac{(n_{HI} + 2z)^2}{(n_{H_2} - z)(n_{I_2} - z)}$$

$$(K-4)z^2 - \{K(n_{H_2} + n_{I_2}) + 4n_{HI}\}z + Kn_{H_2}n_{I_2} - n_{HI}^2 = 0$$

$$866z^2 - 609.80z + 104.36 = 0$$

$$z = \frac{609.80 \pm \sqrt{(-609.80)^2 - 4\times(866)\times(104.36)}}{2\times(866)} = 0.411 \text{ or } 0.293$$

$= 0.293$ because z cannot exceed n_{H_2} so we reject the 0.411 value.

The final composition is therefore $\boxed{0.007\ \text{mol}\ H_2}$, $\boxed{0.107\ \text{mol}\ I_2}$, and $\boxed{0.786\ \text{mol HI}}$.

P6.10 If we knew $\Delta_r H^\ominus$ for the reaction $Cl_2O(g) + H_2O(g) \rightarrow 2\,HOCl(g)$, we could calculate $\Delta_f H^\ominus$ (HOCl) from

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus(HOCl,g) - \Delta_f H^\ominus(Cl_2O,g) - \Delta_f H^\ominus(H_2O,g).$$

We can find $\Delta_r H^\ominus$ if we know $\Delta_r G^\ominus$ and $\Delta_r S^\ominus$, since

$$\Delta_r G^\ominus = \Delta_r H - T\Delta_r S$$

And we can find $\Delta_r G^\ominus$ from the equilibrium constant.

$$K = \exp(-\Delta_r G^\ominus/RT) \quad \text{so} \quad \Delta_r G^\ominus = -RT\ln K$$

$$\begin{aligned}\Delta_r G^\ominus &= -(8.3145\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1})\times(298\text{ K})\ln(8.2\times10^{-2})\\ &= 6.2\text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r G^\ominus + T\Delta_r S^\ominus\\ &= 6.2\text{ kJ mol}^{-1} + (298\text{ K})\times(16.38\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1})\\ &= 11.1\text{ kJ mol}^{-1}\end{aligned}$$

Finally,

$$\begin{aligned}\Delta_f H^\ominus(\text{HOCl,g}) &= \tfrac{1}{2}[\Delta_r H^\ominus + \Delta_f H^\ominus(\text{Cl}_2\text{O,g}) + \Delta_f H^\ominus(\text{H}_2\text{O,g})]\\ &= \tfrac{1}{2}[11.1 + 77.2 + (-241.82)]\text{ kJ mol}^{-1} = \boxed{-76.8\text{ kJ mol}^{-1}}\end{aligned}$$

P6.12 The equilibrium to be considered is (A = gas)

$$\text{A(g,1 bar)} \rightleftharpoons \text{A(soln)} \quad K = \frac{(c/c^\ominus)}{(p/p^\ominus)} = \frac{s}{s^\ominus}$$

$$\Delta_r H^\ominus = -R\times\frac{\mathrm{d}\ln K}{\mathrm{d}\left(\dfrac{1}{T}\right)}\ [6.21(\text{b})]$$

$$\ln K = \ln\left(\frac{s}{s^\ominus}\right) = 2.303\log\left(\frac{s}{s^\ominus}\right)$$

$$\begin{aligned}\Delta_r H^\ominus(\text{H}_2) &= -(2.303)\times(R)\times\frac{\mathrm{d}}{\mathrm{d}\left(\dfrac{1}{T}\right)}\left(-5.39-\frac{768\text{ K}}{T}\right)\\ &= 2.303R\times768\text{ K} = \boxed{+14.7\text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus(\text{CO}) &= -(2.303)\times(R)\times\frac{\mathrm{d}}{\mathrm{d}\left(\dfrac{1}{T}\right)}\left(-5.98-\frac{980\text{ K}}{T}\right)\\ &= 2.303R\times980\text{ K} = \boxed{+18.8\text{ kJ mol}^{-1}}\end{aligned}$$

P6.14 (a) The cell reaction is

$$\text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{H}_2\text{O,l}) = -237.13\text{ kJ mol}^{-1}\ [\text{data table}]$$

$$E^\ominus_{\text{cell}} = -\frac{\Delta_r G^\ominus}{\nu F}\ [6.26] = \frac{+237.13\text{ kJ mol}^{-1}}{(2)\times(96.485\text{ kC mol}^{-1})} = \boxed{+1.23\text{ V}}$$

(b) $\text{C}_4\text{H}_{10}\text{(g)} + \tfrac{13}{2}\text{O}_2\text{(g)} \rightarrow 4\,\text{CO}_2\text{(g)} + 5\,\text{H}_2\text{O(l)}$

$$\begin{aligned}\Delta_r G^\ominus &= 4\Delta_f G^\ominus(\text{CO}_2\text{,g}) + 5\Delta_f G^\ominus(\text{H}_2\text{O,l}) - \Delta_f G^\ominus(\text{C}_4\text{H}_{10}\text{,g})\\ &= [(4)\times(-394.36) + (5)\times(-237.13) - (-17.03)]\text{ kJ mol}^{-1}\ [\text{data tables}]\\ &= -2746.06\text{ kJ mol}^{-1}\end{aligned}$$

In this reaction the number of electrons transferred, v, is not immediately apparent, as in part (a). To find v we break the cell reaction down into half-reactions as follows:

$$\mathrm{R}: \tfrac{13}{2}\,\mathrm{O_2(g)} + 26\,\mathrm{e^-} + 26\,\mathrm{H^+(aq)} \rightarrow 13\,\mathrm{H_2O(l)}$$
$$\mathrm{L}: 4\,\mathrm{CO_2(g)} + 26\,\mathrm{e^-} + 26\,\mathrm{H^+(aq)} \rightarrow \mathrm{C_4H_{10}(g)} + 8\,\mathrm{H_2O(l)}$$
$$\mathrm{R-L}: \mathrm{C_4H_{10}(g)} + \tfrac{13}{2}\,\mathrm{O_2(g)} \rightarrow 4\,\mathrm{CO_2(g)} + 5\,\mathrm{H_2O(l)}$$

Hence, $v = 26$.

Therefore, $E = \dfrac{-\Delta G^\ominus}{vF} = \dfrac{+2746.06\ \mathrm{kJ\ mol^{-1}}}{(26)\times(96.485\ \mathrm{kC\ mol^{-1}})} = \boxed{+1.09\ \mathrm{V}}$

P6.16 $\mathrm{Hg_2Cl_2(s)} + \mathrm{Zn(s)} \rightarrow 2\,\mathrm{Hg(l)} + \mathrm{ZnCl_2(aq)}$ and $v = 2$

(a) $E_{\mathrm{cell}} = E^\ominus_{\mathrm{cell}} - \dfrac{25.693\ \mathrm{mV}}{v}\ln Q$ [6.27,25°C]

$$Q = a(\mathrm{Zn^{2+}})a^2(\mathrm{Cl^-})$$
$$= \{\gamma_+ b(\mathrm{Zn^{2+}})/b^\ominus\}\times\gamma_-^2\{b(\mathrm{Cl^-})/b^\ominus\}^2, \quad \text{where} \quad b(\mathrm{Zn^{2+}}) = b,\ b(\mathrm{Cl^-}) = 2b, \text{ and } \gamma_+\gamma_-^2 = \gamma_\pm^3$$

Therefore, $Q = \gamma_\pm^3 \times 4b^3$ [$b \equiv b/b^\ominus$ here and below]

and $E_{\mathrm{cell}} = E^\ominus_{\mathrm{cell}} - \dfrac{25.693\ \mathrm{mV}}{2}\ln(4b^3\gamma_\pm^3) = E^\ominus_{\mathrm{cell}} - \tfrac{3}{2}\times(25.693\ \mathrm{mV})\times\ln(4^{1/3}b\gamma_\pm)$

$$= \boxed{E^\ominus_{\mathrm{cell}} - (38.54\ \mathrm{mV})\times\ln(4^{1/3}b) - (38.54\ \mathrm{mV})\ln(\gamma_\pm)}$$

(b) $E^\ominus_{\mathrm{cell}} = E^\ominus(\mathrm{Hg_2^{2+}/Hg}) - E^\ominus(\mathrm{Zn^{2+}/Zn}) = +0.2676\ \mathrm{V} - (-0.7628\ \mathrm{V}) = \boxed{1.0304\ \mathrm{V}}$

(c) $\Delta_r G = -vFE_{\mathrm{cell}} = -(2)\times(9.6485\times10^4\ \mathrm{C\ mol^{-1}})\times(1.2272\ \mathrm{V}) = \boxed{-236.81\ \mathrm{kJ\ mol^{-1}}}$

$\Delta_r G^\ominus = -vFE^\ominus_{\mathrm{cell}} = -(2)\times(9.6485\times10^4\ \mathrm{C\ mol^{-1}})\times(1.0304\ \mathrm{V}) = \boxed{-198.84\ \mathrm{kJ\ mol^{-1}}}$

$\ln K = -\dfrac{\Delta_r G^\ominus}{RT} = \dfrac{1.9884\times10^5\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298.15\ \mathrm{K})} = 80.211$ so $K = \boxed{6.84\times10^{34}}$

(d) From part (a):

$$1.2272\ \mathrm{V} = 1.0304\ \mathrm{V} - (38.54\ \mathrm{mV})\times\ln(4^{1/3}\times0.0050) - (38.54\ \mathrm{mV})\times\ln\gamma_\pm$$

$\ln\gamma_\pm = -\dfrac{(1.2272\ \mathrm{V}) - (1.0304\ \mathrm{V}) - (0.186\bar{4}\ \mathrm{V})}{0.03854\ \mathrm{V}} = -0.269\bar{8}$ so $\gamma_\pm = \boxed{0.763}$

(e) $\log\gamma_\pm = -|z_-z_+|AI^{1/2}$ [5.75]

$I = \tfrac{1}{2}\sum_i z_i^2(b_i/b^\ominus)$ [5.76]

where $b(\mathrm{Zn^{2+}}) = b = 0.0050\ \mathrm{mol\ kg^{-1}}$ and $b(\mathrm{Cl^-}) = 2b = 0.010\ \mathrm{mol\ kg^{-1}}$

Thus, $I = \tfrac{1}{2}[(4)\times(0.0050) + (0.010)] = 0.015$

$\log\gamma_\pm = -(2)\times(0.509)\times(0.015)^{1/2} = -0.12\bar{5}$ so $\gamma_\pm = \boxed{0.75}$

This compares remarkably well to the value obtained from experimental data in part (d).

(f) $$\Delta_r S = -\left(\frac{\partial \Delta_r G}{\partial T}\right)_p$$

$$= \nu F\left(\frac{\partial E}{\partial T}\right)_p [6.36] = (2)\times(9.6485\times10^4\,\mathrm{C\,mol^{-1}})\times(-4.52\times10^{-4}\,\mathrm{V\,K^{-1}})$$

$$= \boxed{-87.2\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

$$\Delta_r H = \Delta_r G + T\Delta_r S = (-236.81\,\mathrm{kJ\,mol^{-1}}) + (298.15\,\mathrm{K})\times(-87.2\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$$= \boxed{-262.4\ \mathrm{kJ\,mol^{-1}}}$$

P6.18 $\mathrm{Pt}|\mathrm{H_2}(\mathrm{g},p^\ominus)|\mathrm{NaOH}(\mathrm{aq},0.01000\ \mathrm{mol\,kg^{-1}}),\mathrm{NaCl}(\mathrm{aq},0.01125\ \mathrm{mol\,kg^{-1}})|\mathrm{AgCl(s)}|\mathrm{Ag(s)}$

$\mathrm{H_2(s)} + 2\,\mathrm{AgCl(s)} \rightarrow 2\,\mathrm{Ag(s)} + 2\,\mathrm{Cl^-(aq)} + 2\,\mathrm{H^+(aq)}$, where $\nu = 2$

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{2F}\ln\{a(\mathrm{H^+})a(\mathrm{Cl^-})\}^2\ [6.27 \text{ and } 6.12(b)]$$

$$= E^\ominus_{\text{cell}} - \frac{RT}{F}\ln\{a(\mathrm{H^+})a(\mathrm{Cl^-})\} = E^\ominus - \frac{RT}{F}\ln\frac{K_w a(\mathrm{Cl^-})}{a(\mathrm{OH^-})} = E^\ominus - \frac{RT}{F}\ln\frac{K_w\gamma_\pm b(\mathrm{Cl^-})}{\gamma_\pm b(\mathrm{OH^-})}$$

$$= E^\ominus_{\text{cell}} - \frac{RT}{F}\ln\frac{K_w b(\mathrm{Cl^-})}{b(\mathrm{OH^-})} = E^\ominus - \frac{RT}{F}\ln K_w - \frac{RT}{F}\ln\frac{b(\mathrm{Cl^-})}{b(\mathrm{OH^-})}$$

$$= E^\ominus_{\text{cell}} + (2.303)\frac{RT}{F}\times \mathrm{p}K_w - \frac{RT}{F}\ln\frac{b(\mathrm{Cl^-})}{b(\mathrm{OH^-})}\left(\mathrm{p}K_w = -\log K_w = \frac{-\ln K_w}{2.303}\right)$$

$$\text{Hence, } \mathrm{p}K_w = \frac{E_{\text{cell}} - E^\ominus_{\text{cell}}}{2.303RT/F} + \frac{\ln\left(\dfrac{b(\mathrm{Cl^-})}{b(\mathrm{OH^-})}\right)}{2.303} = \frac{E_{\text{cell}} - E^\ominus_{\text{cell}}}{2.303RT/F} + 0.05114$$

Using information from the data tables we find that:

$$E^\ominus_{\text{cell}} = E^\ominus_{\mathrm{R}} - E^\ominus_{\mathrm{L}} = E^\ominus(\mathrm{AgCl,Ag}) - E^\ominus(\mathrm{H^+/H_2}) = +0.22\ \mathrm{V} - 0 = +0.22\ \mathrm{V}$$

This value does not have the precision needed for computations with the high precision data of this problem. Consequently, we will use the more precise value found in the *CRC Handbook of Chemistry and Physics* (71st edn): $E^\ominus_{\text{cell}} = 0.22233\ \mathrm{V}$.

We then draw up the following table:

$\theta/{}^\circ\mathrm{C}$	20.0	25.0	30.0
$E_{\text{cell}}/\mathrm{V}$	1.04774	1.04864	1.04942
$\ln(10)RTF^{-1}/\mathrm{V}$	0.058168	0.059160	0.060152
$\mathrm{p}K_w$	$\boxed{14.24}$	$\boxed{14.02}$	$\boxed{13.80}$

$$\frac{\mathrm{d}\ln K_w}{\mathrm{d}T} = \frac{\Delta_r H^\ominus}{RT^2}\ [6.21(a)]$$

Hence, $\Delta_r H^\ominus = -(2.303)RT^2 \dfrac{\mathrm{d}}{\mathrm{d}T}(\mathrm{p}K_w)$

then with $\dfrac{\mathrm{dp}K_w}{\mathrm{d}T} \approx \dfrac{\Delta \mathrm{p}K_w}{\Delta T}$

$$\Delta_r H^\ominus \approx -(2.303) \times (8.314\ \mathrm{J\ K^{-1}\,mol^{-1}}) \times (298.15\ \mathrm{K})^2 \times \frac{13.80 - 14.24}{10\ \mathrm{K}}$$

$$= \boxed{+74.9\ \mathrm{kJ\ mol^{-1}}}$$

$$\Delta_r G^\ominus = -RT \ln K_w = 2.303RT \times \mathrm{p}K_w = \boxed{+80.0\ \mathrm{kJ\ mol^{-1}}}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \boxed{-17.1\ \mathrm{J\ K^{-1}\,mol^{-1}}}$$

P6.20 The method of the solution is first to determine $\Delta_r G^\ominus$, $\Delta_r H^\ominus$, and $\Delta_r S^\ominus$ for the cell reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{AgCl(s)} \rightarrow \mathrm{Ag(s)} + \mathrm{HCl(aq)}$$

and then, from the values of these quantities and the known values of $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $S^\ominus$, for all the species other than $\mathrm{Cl^-(aq)}$, to calculate $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $S^\ominus$ for $\mathrm{Cl^-(aq)}$.

$$\Delta_r G^\ominus = -\nu F E^\ominus$$

At 298.15 K (25.00°C)

$$E^\ominus/\mathrm{V} = (0.23659) - (4.8564 \times 10^{-4}) \times (25.00) - (3.4205 \times 10^{-6}) \times (25.00)^2 + (5.869 \times 10^{-9}) \times (25.00)^3 = +0.22240\ \mathrm{V}.$$

Therefore, $\Delta_r G^\ominus = -(96.485\ \mathrm{kC\ mol^{-1}}) \times (0.22240\ \mathrm{V}) = -21.46\ \mathrm{kJ\ mol^{-1}}$

$$\Delta_r S^\ominus = -\left(\frac{\partial \Delta_r G^\ominus}{\partial T}\right)_p = \nu F\left(\frac{\partial E^\ominus}{\partial T}\right)_p = \nu F\left(\frac{\partial E^\ominus}{\partial \theta}\right)_p \frac{{}^\circ\mathrm{C}}{\mathrm{K}}\ [\mathrm{d}\theta/{}^\circ\mathrm{C} = \mathrm{d}T/K] \quad \text{(a)}$$

$$(\partial E^\ominus/\partial\theta)_p/\mathrm{V} = (-4.8564 \times 10^{-4}/{}^\circ\mathrm{C}) - (2) \times (3.4205 \times 10^{-6}\theta/({}^\circ\mathrm{C})^2) + (3) \times (5.869 \times 10^{-9}\theta^2/({}^\circ\mathrm{C})^3)$$

$$(\partial E^\ominus/\partial\theta)_p/(\mathrm{V}\,{}^\circ\mathrm{C}^{-1}) = (-4.8564 \times 10^{-4}) - (6.8410 \times 10^{-6}(\theta/{}^\circ\mathrm{C})) + (1.7607 \times 10^{-8}(\theta/{}^\circ\mathrm{C})^2)$$

Therefore, at 25°C,

$$(\partial E^\ominus/\partial\theta)_p = -6.4566 \times 10^{-4}\ \mathrm{V/{}^\circ C}$$

and

$$(\partial E^\ominus/\partial\theta)_p = (-6.4566 \times 10^{-4}\ \mathrm{V/{}^\circ C}) \times ({}^\circ\mathrm{C/K}) = -6.4566 \times 10^{-4}\ \mathrm{V\ K^{-1}}$$

Hence, from equation (a)

$$\Delta_r S^\ominus = (-96.485\ \mathrm{kC\ mol^{-1}}) \times (6.4566 \times 10^{-4}\ \mathrm{V\ K^{-1}}) = -62.30\ \mathrm{J\ K^{-1}\,mol^{-1}}$$

and $\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$

$$= -(21.46\ \mathrm{kJ\ mol^{-1}}) + (298.15\ \mathrm{K}) \times (-62.30\ \mathrm{J\ K^{-1}\,mol^{-1}}) = -40.03\ \mathrm{kJ\ mol^{-1}}$$

For the cell reaction $\tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{AgCl(s)} \rightarrow \mathrm{Ag(s)} + \mathrm{HCl(aq)}$

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\mathrm{H^+}) + \Delta_f G^\ominus(\mathrm{Cl^-}) - \Delta_f G^\ominus(\mathrm{AgCl})$$
$$= \Delta_f G^\ominus(\mathrm{Cl^-}) - \Delta_f G^\ominus(\mathrm{AgCl}) \quad [\Delta_f G^\ominus(\mathrm{H^+}) = 0$$

Hence, $\Delta_f G^{\ominus}(\text{Cl}^-) = \Delta_r G^{\ominus} + \Delta_f G^{\ominus}(\text{AgCl}) = (-21.46 - 109.79)\ \text{kJ mol}^{-1}$

$$= \boxed{-131.25\ \text{kJ mol}^{-1}}$$

Similarly, $\Delta_f H^{\ominus}(\text{Cl}^-) = \Delta_r H^{\ominus} + \Delta_f H^{\ominus}(\text{AgCl}) = (-40.03 - 127.07)\ \text{kJ mol}^{-1}$

$$= \boxed{-167.10\ \text{kJ mol}^{-1}}$$

For the entropy of Cl^- in solution we use

$$\Delta_r S^{\ominus} = S^{\ominus}(\text{Ag}) + S^{\ominus}(\text{H}^+) + S^{\ominus}(\text{Cl}^-) - \tfrac{1}{2}S^{\ominus}(\text{H}_2) - S^{\ominus}(\text{AgCl})$$

with $S^{\ominus}(\text{H}^+) = 0$. Then,

$$S^{\ominus}(\text{Cl}^-) = \Delta_r S^{\ominus} - S^{\ominus}(\text{Ag}) + \tfrac{1}{2}S^{\ominus}(\text{H}_2) + S^{\ominus}(\text{AgCl})$$

$$= \{(-62.30) - (42.55) + \tfrac{1}{2}\times(130.68) + (96.2)\}\ \text{J K}^{-1}\,\text{mol}^{-1} = \boxed{+56.7\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

Solutions to theoretical problems

P6.22 We draw up the following table using the stoichiometry $\text{A} + 3\,\text{B} \rightarrow 2\,\text{C}$ and $\Delta n_J = \nu_J \xi$.

	A	B	C	Total
Initial amount/mol	1	3	0	4
Change, Δn_J/mol	$-\xi$	-3ξ	$+2\xi$	
Equilibrium amount/mol	$1-\xi$	$3(1-\xi)$	2ξ	$2(2-\xi)$
Mole fraction	$\dfrac{1-\xi}{2(2-\xi)}$	$\dfrac{3(1-\xi)}{2(2-\xi)}$	$\dfrac{\xi}{2-\xi}$	1

$$K = \frac{(p_C/p^{\ominus})^2}{(p_A/p^{\ominus})(p_B/p^{\ominus})^3} = \frac{x_C^2}{x_A x_B^3}\times\left(\frac{p^{\ominus}}{p}\right)^2 = \frac{\xi^2}{(2-\xi)^2}\times\frac{2(2-\xi)}{1-\xi}\times\frac{2^3(2-\xi)^3}{3^3(1-\xi)^3}\times\left(\frac{p^{\ominus}}{p}\right)^2$$

$$= \frac{16(2-\xi)^2\xi^2}{27(1-\xi)^4}\times\left(\frac{p^{\ominus}}{p}\right)^2$$

Since K is independent of the pressure

$$\frac{(2-\xi)^2\xi^2}{(1-\xi)^4} = a^2\left(\frac{p}{p^{\ominus}}\right)^2, \quad \text{where} \quad a^2 = \frac{27}{16}K, \text{ a constant}$$

Therefore, $(2-\xi)\xi = a\left(\dfrac{p}{p^{\ominus}}\right)\times(1-\xi)^2$

$$\left(1+\frac{ap}{p^{\ominus}}\right)\xi^2 - 2\left(1+\frac{ap}{p^{\ominus}}\right)\xi + \frac{ap}{p^{\ominus}} = 0$$

which solves to $\boxed{\xi = 1 - \left(\dfrac{1}{1+ap/p^{\ominus}}\right)^{1/2}}$.

We choose the root with the negative sign because ξ lies between 0 and 1. The variation of ξ with p is shown in Figure 6.2.

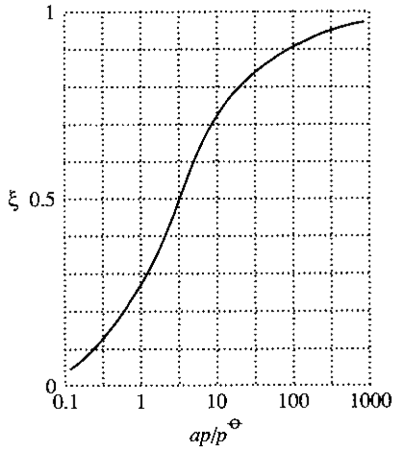


Figure 6.2

P6.24 For a gas-phase reaction the equilibrium constant is given by the expression

$$K=\left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}}[6.13]=\left(\prod_J(\gamma_J p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}=\left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J(p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$=K_\gamma K_p,\quad \text{where}\quad K_\gamma=\left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\quad\text{and}\quad K_p=\left(\prod_J(p_J/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma=1$. Additionally, $p_J=n_JRT/V=[J]RT$. Substitution gives

$$K=K_p=\left(\prod_J([J]RT/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}=\left(\prod_J([J]/c^\ominus)^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J(c^\ominus RT/p^\ominus)^{\nu_J}\right)_{\text{equilibrium}}$$

$$=K_c(c^\ominus RT/p^\ominus)^{\Delta\nu},\quad\text{where}\quad K_c=\left(\prod_J([J]/c^\ominus)^{\nu_J}\right)_{\text{equilibrium}}\quad\text{and}\quad \Delta\nu=\sum_J\nu_J$$

Thus, $\boxed{K_c=K\times(c^\ominus RT/p^\ominus)^{-\Delta\nu}}$.

The above relationship gives the temperature dependence of K_c provided that the temperature dependence of K is known. In the case for which we know $\Delta_rH^\ominus$, and it is a constant, and we know the value of the equilibrium constant at the temperature T_{ref}, we use eqn 6.23 to calculate the value of K at temperature T:

$$\ln K=\ln K_{\text{ref}}-\frac{\Delta_rH^\ominus}{R}\left(\frac{1}{T}-\frac{1}{T_{\text{ref}}}\right)[6.23]\quad\text{or}\quad K=K_{\text{ref}}\,e^{-\frac{\Delta_rH^\ominus}{R}\left(\frac{1}{T}-\frac{1}{T_{\text{ref}}}\right)}$$

Alternatively, if we know (a) the coefficients a, b, and c for reactants and products in the expression for the molar heat capacity listed in Table 2.2, (b) $\Delta_fG^\ominus(T_{\text{ref}})$, and (c) $\Delta_fS^\ominus(T_{\text{ref}})$, we calculate $\Delta_fG^\ominus(T)$

with the expression derived in Problem 6.23. This gives us $K(T)$ through the expression $K = e^{-\Delta_r G^\ominus/RT}$ [6.14] after which we calculate $K_c(T)$ with the above relationship. Recognize, however, that this finely tuned effort may not be justified in face of the perfect gas assumption.

Solutions to applications: biology, environmental science, and chemical engineering

6.26 $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ [6.10]

In eqn 6.10 molar solution concentrations are used with 1 M standard states ($c^\ominus = 1$ mol dm^{-3}). The standard state ($^\ominus$) pH equals zero in contrast to the biological standard state ($^\oplus$) of pH 7. For the ATP hydrolysis

$$\text{ATP(aq)} + H_2O(l) \rightarrow \text{ADP(aq)} + P_i^-(aq) + H_3O^+(aq)$$

we can calculate the standard state free energy given the biological standard free energy of about -31 kJ mol^{-1} (*Impact* 6.1).

$$\Delta_r G^\oplus = \Delta_r G^\ominus + RT \ln Q^\oplus \ [6.10]$$

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r G^\oplus - RT \ln Q^\oplus \\ &= -31\ \text{kJ mol}^{-1} - (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (310\ \text{K}) \ln(10^{-1}\ \text{M}/1\ \text{M}) \\ &= +11\ \text{kJ mol}^{-1}\end{aligned}$$

This calculation shows that under standard conditions the hydrolysis of ATP is not spontaneous! It is endergonic.

The calculation of the ATP hydrolysis free energy with the cell conditions pH = 7, [ATP] = [ADP] = $[P_i^-] = 1.0 \times 10^{-6}$ M, is interesting.

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q = \Delta_r G^\ominus + RT \ln\left(\frac{[\text{ADP}] \times [P_i^-] \times [H^+]}{[\text{ATP}] \times (1\ \text{M})^2}\right)$$

$$\begin{aligned}&= +11\ \text{kJ mol}^{-1} + (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (310\ \text{K}) \ln(10^{-6} \times 10^{-7}) \\ &= -66\ \text{kJ mol}^{-1}\end{aligned}$$

The concentration conditions in biological cells make the hydrolysis of ATP spontaneous and very exergonic. A maximum of 66 kJ of work is available to drive coupled chemical reactions when a mole of ATP is hydrolysed.

6.28 Yes, a bacterium can evolve to utilize the ethanol/nitrate pair to exergonically release the free energy needed for ATP synthesis. The ethanol reductant may yield any of the following products:

$$\underset{\text{ethanol}}{CH_3CH_2OH} \rightarrow \underset{\text{ethanal}}{CH_3CHO} \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH} \rightarrow CO_2 + H_2O$$

The nitrate oxidant may receive electrons to yield any of the following products:

$$\underset{\text{nitrate}}{NO_3^-} \rightarrow \underset{\text{nitrite}}{NO_2^-} \rightarrow \underset{\text{dinitrogen}}{N_2} \rightarrow \underset{\text{ammonia}}{NH_3}$$

Oxidation of two ethanol molecules to carbon dioxide and water can transfer eight electrons to nitrate during the formation of ammonia. The half-reactions and net reaction are:

$$2\,[CH_3CH_2OH(l) \rightarrow 2\,CO_2(g) + H_2O(l) + 4\,H^+(aq) + 4\,e^-]$$

$$NO_3^-(aq) + 9\,H^+(aq) + 8\,e^- \rightarrow NH_3(aq) + 3\,H_2O(l)$$

$$2\,CH_3CH_2OH(l) + H^+(aq) + NO_3^-(aq) \rightarrow 4\,CO_2(g) + 5\,H_2O(l) + NH_3(aq)$$

$\Delta_r G^{\ominus} = -2331.29$ kJ for the reaction as written (a data table calculation). Of course, enzymes must evolve that couple this exergonic redox reaction to the production of ATP, which would then be available for carbohydrate, protein, lipid, and nucleic acid synthesis.

P6.30 (a) The equilibrium constant is given by

$$K = \exp\left(\frac{-\Delta_r G^{\ominus}}{RT}\right) = \exp\left(\frac{-\Delta_r H^{\ominus}}{RT}\right)\exp\left(\frac{\Delta_r S^{\ominus}}{R}\right)$$

so $\ln K = -\frac{-\Delta_r H^{\ominus}}{RT} + \frac{\Delta_r S^{\ominus}}{R}$

A plot of ln K against $1/T$ should be a straight line with a slope of $-\Delta_r H^{\ominus}/R$ and a y-intercept of $\Delta_r S^{\ominus}/R$ (Figure 6.3).

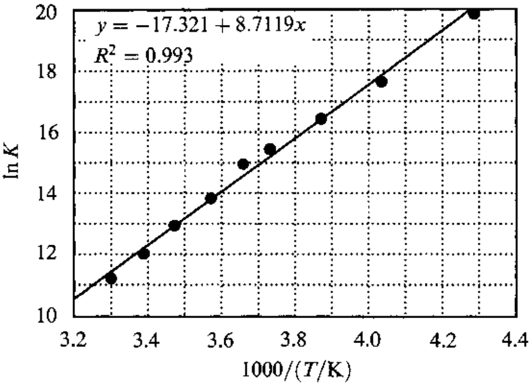


Figure 6.3

So, $\Delta_r H^{\ominus} = -R \times \text{slope} = -(8.3145 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}) \times (8.71 \times 10^3\ \text{K})$

$$= \boxed{-72.4\ \text{kJ mol}^{-1}}$$

and $\Delta_r S^{\ominus} = R \times \text{intercept} = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (-17.3) = \boxed{-144\ \text{J K}^{-1}\ \text{mol}^{-1}}$

(b) $\Delta_r H^{\ominus} = \Delta_f H^{\ominus}((ClO)_2) - 2\,\Delta_f H^{\ominus}(ClO)$, so $\Delta_f H^{\ominus}((ClO)_2) = \Delta_r H^{\ominus} + 2\,\Delta_f H^{\ominus}(ClO)$

$$\Delta_f H^{\ominus}((ClO)_2) = [-72.4 + 2(101.8)]\ \text{kJ mol}^{-1} = \boxed{+131.2\ \text{kJ mol}^{-1}}$$

$$S^{\ominus}((ClO)_2) = [-144 + 2(226.6)]\text{J K}^{-1}\ \text{mol}^{-1} = \boxed{+309.2\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

6.32 $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g) \quad \Delta\nu = \sum_J \nu_J = -1$

This is the ammonia formation reaction for which we find the standard reaction thermodynamic functions in the text data tables:

$$\Delta_r H^\circ(298\text{ K}) = -46.11\text{ kJ} \quad \text{and} \quad \Delta_r S^\circ(298\text{ K}) = -99.38\text{ J K}^{-1}$$

Use text data tables to establish functions for the constant pressure heat capacity of reactants and products. Define a function $\Delta_r C_p^\circ(T)$ that makes it possible to calculate $\Delta_r C_p$ at 1 bar and any temperature (eqns 2.36b and 2.25). Define functions that make it possible to calculate the reaction enthalpy and entropy at 1 bar and any temperature (eqns 2.36a and 3.22).

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(298) + \int_{298.15\text{ K}}^{T} \Delta_r C_p^\circ(T)\mathrm{d}T$$

$$\Delta_r S^\circ(T) = \Delta_r S^\circ(298) + \int_{298.15\text{ K}}^{T} \frac{\Delta_r C_p^\circ(T)}{T}\mathrm{d}T$$

(i) For a perfect gas reaction mixture $\Delta_r H$ is independent of pressure at constant temperature. Consequently, $\Delta_r H(T,p) = \Delta_r H^\circ(T)$. The pressure dependence of the reaction entropy may be evaluated with the expression:

$$\Delta_r S(T,p) = \Delta_r S^\circ(T) + \sum_{\text{Products-Reactants},i} \nu_i \int_{1\text{ bar}}^{p} \left(\frac{\partial S_{m,i}}{\partial p}\right)_T \mathrm{d}p$$

$$= \Delta_r S^\circ(T) - \sum_{\text{Products-Reactants},i} \nu_i \int_{1\text{ bar}}^{p} \left(\frac{\partial V_{m,i}}{\partial T}\right)_p \mathrm{d}p \text{ (Table 3.5)}$$

$$= \Delta_r S^\circ(T) - \sum_{\text{Products-Reactants},i} \nu_i \int_{1\text{ bar}}^{p} \frac{R}{p}\mathrm{d}p$$

$$= \Delta_r S^\circ(T) - \left[\sum_{\text{Products-Reactants},i} \nu_i\right] R\ln\left(\frac{p}{1\text{ bar}}\right) = \Delta_r S^\circ(T) - (-1)\, R\ln\left(\frac{p}{1\text{ bar}}\right)$$

$$= \Delta_r S^\circ(T) + R\ln\left(\frac{p}{1\text{ bar}}\right)$$

The above two equations make it possible to calculate $\Delta_r G(T,p)$:

$$\Delta_r G(T,p) = \Delta_r H(T,p) - T\Delta_r S(T,p)$$

Once the above functions have been defined on a scientific calculator or with mathematical software on a computer, the root function may be used to evaluate pressure, where $\Delta_r G(T,p) = -500$ J at a given temperature.

(a) and (b) perfect gas mixture:

For $T = (450 + 273.15)\text{K} = 723.15$ K, root($\Delta_r G(723.15\text{ K},p) + 500$ J) = $\boxed{156.5\text{ bar}}$

For $T = (400 + 273.15)\text{K} = 673.15$ K, root($\Delta_r G(673.15\text{ K},p) + 500$ J) = $\boxed{81.8\text{ bar}}$

(ii) For a van der Waals gas mixture $\Delta_r H$ does depend on pressure. The calculation equation is:

$$\Delta_r H(T,p) = \Delta_r H^\circ(T) + \sum_{\text{Products--Reactants,i}} \nu_i \int_{1\,\text{bar}}^{p} \left(\frac{\partial H_{\text{m,i}}}{\partial p}\right)_T \mathrm{d}p$$

[the sum involves the i = 1, 2, 3 gases (NH_3, N_2, or H_2)]

$$= \Delta_r H^\circ(T) + \sum_{\text{Products--Reactants,i}} \nu_i \int_{1\,\text{bar}}^{p} \left[V_{\text{m,i}} - T\left(\frac{\partial V_{\text{m,i}}}{\partial T}\right)_p\right] \mathrm{d}p$$

[the equation of this substitution is proven below*]

where $(\partial V_{\text{m,i}}/\partial T)_p = R(V_{\text{m,i}} - b_i)^{-1}(RT(V_{\text{m,i}} - b_i)^{-2} - 2a_i V_{\text{m,i}}^{-3})^{-1}$ for each gas i (NH_3, N_2, or H_2)

and $V_{\text{m,i}}(T,p) = \text{root}\left(p - \dfrac{RT}{V_{\text{m,i}} - b_i} + \dfrac{a_i}{V_{\text{m,i}}^2}\right)$

The functional equation for $\Delta_r S$ calculations is:

$$\Delta_r S(T,p) = \Delta_r S^\circ(T) - \sum_{\text{Products--Reactants,i}} \nu_i \int_{1\,\text{bar}}^{p} \left(\frac{\partial V_{\text{m,i}}}{\partial T}\right)_p \mathrm{d}p$$

where $(\partial V_{\text{m,i}}/\partial T)_p$ and $V_{\text{m,i}}(T,p)$ are calculated as described above. As usual,

$$\Delta_r G(T,p) = \Delta_r H(T,p) - T\Delta_r S(T,p)$$

(a) and (b) van der Waals gas mixture:

For $T = 723.15$ K, root($\Delta_r G(723.15\ \text{K},p) + 500$ J) = $\boxed{132.5\ \text{bar}}$

For $T = 673.15$ K, root($\Delta_r G(673.15\ \text{K},p) + 500$ J) = $\boxed{73.7\ \text{bar}}$

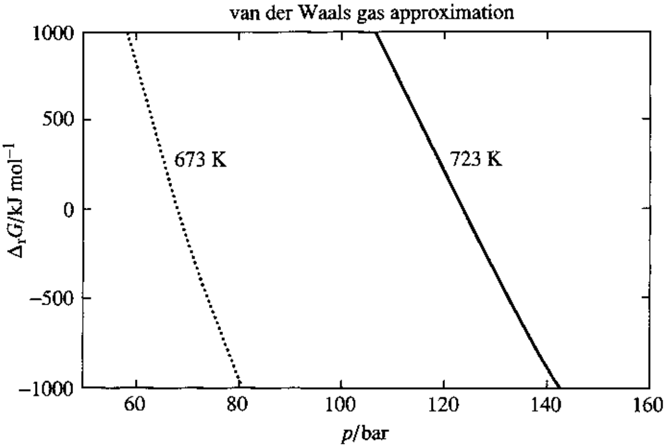


Figure 6.4

(c) $\Delta_r G(T,p)$ isotherms (see Figure 6.4) $\boxed{\text{confirm}}$ Le Chatelier's principle. Along an isotherm, $\Delta_r G$ decreases as pressure increases. This corresponds to a shift to the right in the reaction equation and reduces the stress by shifting to the side that has fewer total moles of gas. Additionally, the reaction is exothermic, so Chatelier's principle predicts a shift to the left with an increase in temperature. The isotherms confirm this as an increase in $\Delta_r G$ as temperature is increased at constant pressure.

Note: There are many thermodynamic equations that are very useful when deriving desired computation equations. One of them (used above) is: $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$. To prove this relationship, first use an identity of partial derivatives that involves a change of variable

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S$$

We will be able to identify some of these terms if we examine an expression for $\mathrm{d}H$ analogous to the fundamental equation of thermodynamics [3.46]. From the definition of enthalpy, we have:

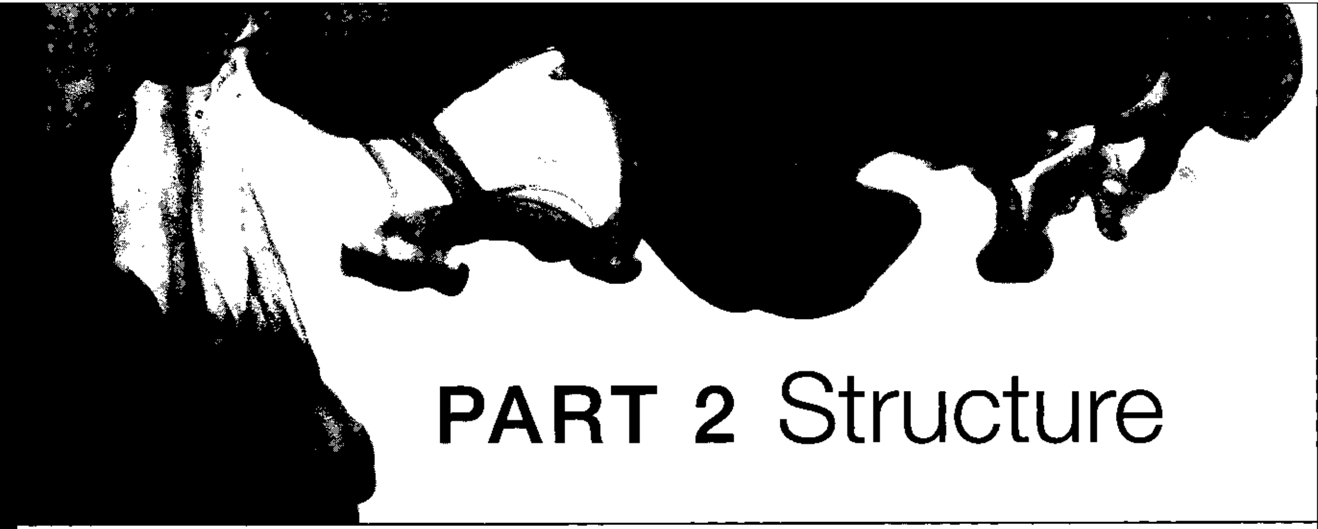
$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p = T\mathrm{d}S - p\mathrm{d}V\,[3.46] + p\mathrm{d}V + V\mathrm{d}p = T\mathrm{d}S - V\mathrm{d}p$$

Compare this expression to the exact differential of H considered as a function of S and p:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p$$

Thus, $\left(\frac{\partial H}{\partial S}\right)_p = T,\ \left(\frac{\partial H}{\partial p}\right)_S = V$ [$\mathrm{d}H$ exact]

Substitution yields $\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = \boxed{-T\left(\frac{\partial V}{\partial T}\right)_p + V}$ [Maxwell relation]



PART 2 Structure

7 Quantum theory: introduction and principles

Answers to discussion questions

D7.2 A successful theory of black-body radiation must be able to explain the energy density distribution of the radiation as a function of wavelength, in particular the observed drop to zero as $\lambda \to 0$. Classical theory predicts the opposite. However, if we assume, as did Planck, that the energy of the oscillators that constitute electromagnetic radiation are quantized according to the relationship $E = nh\nu = nhc/\lambda$, where the **quantum number *n*** can equal zero or any positive integer, we see that at short wavelengths the energy of the oscillators is very large. This energy is too large for the walls to supply it, so the short-wavelength oscillators remain unexcited. The effect of quantization is to reduce the contribution to the total energy emitted by the black-body from the high-energy short-wavelength oscillators, for they cannot be sufficiently excited with the energy available.

D7.4 By **wave–particle duality** we mean that in some experiments an entity behaves as a wave, while in other experiments the same entity behaves as a particle. Electromagnetic radiation behaves as a wave in reflection and refraction experiments but it behaves as particulate photons in absorption and emission spectroscopy. Electrons behave as waves in diffraction experiments but as particles in the photoelectric effect. Consequences are especially important for small fundamental particles like electrons, atoms, and molecules. One consequence is the impossibility of precisely and simultaneously specifying complementary observables like position and momentum for fundamental particles. It is also impossible to specify the simultaneous energy and timing of an event. Rather, the multiplied uncertainties of **complementary observables**, such as x and p_x or E and t, must always be greater than, or equal to, $\hbar/2$ (i.e. the **Heisenberg uncertainty principle** of eqn 7.39a). Quantum theory shows that, because of wave–particle duality, it is necessary to specify the wavefunction ψ of fundamental particles and to use the tenets, which we call postulates, of quantum mechanics to interpret their behavior and observable properties. The basic postulates are:

Postulate I, Section 7.3. The state of the system is described as fully as possible by the wavefunction $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots)$, where $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots$ are the spatial coordinates of all particles $(1, 2, \ldots)$ in the system.

Postulate II, the **Born interpretation** Section 7.4. For a system described by the wavefunction $\psi(\boldsymbol{r})$, the probability of finding the particle in the volume $\mathrm{d}\tau$ is proportional to $|\psi|^2\mathrm{d}\tau = \psi^*\psi\mathrm{d}\tau$. The constant of proportionality, the **normalization constant**, is chosen so that the integral $\int_{\text{all space}} |\psi|^2\,\mathrm{d}\tau$ equals 1.

Postulate III, Section 7.5. For each observable property Ω of a system there is a corresponding operator $\hat{\Omega}$ built from the following position and linear momentum operators.

$$\hat{x} = x\times \quad \text{and} \quad \hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\ [7.29]$$

Postulate IV, eqns 7.27a and 7.28b. If the system is described by a wavefunction ψ that is an eigenfunction of $\hat{\Omega}$ such that $\hat{\Omega}\psi = \omega\psi$, then the outcome of a measurement of Ω will be the eigenvalue ω.

Postulate V, Section 7.5e. When the value of an observable Ω is measured for a system that is described by a linear combination of eigenfunctions of $\hat{\Omega}$, with coefficients c_k, each measurement gives one of the eigenvalues ω_k of $\hat{\Omega}$ with a probability proportional to $|c_k|^2$.

D7.6 If the wavefunction describing the linear momentum of a particle is precisely known, the particle has a definite state of linear momentum; but then according to the uncertainty principle (eqn 7.39a), the position of the particle is completely unknown. Conversely, if the position of a particle is precisely known, its linear momentum cannot be described by a single wavefunction. Rather, the wavefunction is a superposition of many wavefunctions, each corresponding to a different value for the linear momentum. All knowledge of the linear momentum of the particle is lost when its position is specified exactly. In the limit of an infinite number of superposed wavefunctions, the wavepacket turns into the sharply spiked packet shown in Figure 7.30. But the requirement of the superposition of an infinite number of momentum wavefunctions in order to locate the particle means a complete lack of knowledge of the momentum.

Solutions to exercises

E7.1(b) The de Broglie relationship is $\lambda = \dfrac{h}{p}\ [7.16] = \dfrac{h}{mv}$.

Hence, $v = \dfrac{h}{m_p\lambda} = \dfrac{6.626\times10^{-34}\ \mathrm{J\ s}}{(1.673\times10^{-27}\ \mathrm{kg})\times(3.0\times10^{-2}\ \mathrm{m})} = \boxed{1.3\times10^{-5}\ \mathrm{m\ s^{-1}}}$, which is extremely slow!

E7.2(b) The momentum of a photon is

$$p = \frac{h}{\lambda}\ [7.16] = \frac{6.626\times10^{-34}\ \mathrm{J\ s}}{350\times10^{-9}\ \mathrm{m}} = \boxed{1.89\times10^{-27}\ \mathrm{kg\ m\ s^{-1}}}$$

The momentum of a particle is $p = mv$ so the speed of a hydrogen molecule that has the above momentum is

$$v = \frac{p}{m_{\mathrm{H_2}}} = \frac{p}{M_{\mathrm{H_2}}/N_{\mathrm{A}}} = \frac{1.89\times10^{-27}\ \mathrm{kg\ m\ s^{-1}}}{(2.016\times10^{-3}\ \mathrm{kg\ mol^{-1}}/6.022\times10^{23}\ \mathrm{mol^{-1}})} = \boxed{0.565\ \mathrm{m\ s^{-1}}}$$

E7.3(b) The desired uncertainty in the electron momentum is

$$\begin{aligned}\Delta p &= 1.00\times10^{-5}\ p = 1.00\times10^{-5}\ m_{\mathrm{e}}v\\ &= (1.00\times10^{-5})\times(9.109\times10^{-31}\ \mathrm{kg})\times(995\times10^{3}\ \mathrm{m\ s^{-1}})\\ &= 9.06\times10^{-30}\ \mathrm{kg\ m\ s^{-1}}\end{aligned}$$

Thus, the minimum uncertainty in position must be

$$\Delta x = \frac{\hbar}{2\Delta p}\,[7.39\text{a}] = \frac{1.055\times10^{-34}\ \text{J s}}{2\times(9.06\times10^{-30}\ \text{kg m s}^{-1})} = \boxed{5.82\ \mu\text{m}}$$

7.4(b)

$$E = h\nu = \frac{hc}{\lambda}\,[7.14 \text{ and } 7.1] = \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{\lambda} = \frac{1.986\times10^{-25}\ \text{J m}}{\lambda}$$

$$E_{\text{m}} = N_{\text{A}}E = \frac{N_{\text{A}}hc}{\lambda} = \frac{0.1196\ \text{J m}}{\lambda}$$

We can therefore draw up the following table:

λ	E/J	$E_{\text{m}}/(\text{kJ mol}^{-1})$
(a) 200×10^{-9}	9.93×10^{-19}	598
(b) 150×10^{-12}	1.32×10^{-15}	7.97×10^{5}
(c) 1.00×10^{-2}	1.99×10^{-23}	0.012

E7.5(b) On absorption of a photon by a free helium-4 atom, the law of conservation of energy requires that the acquired kinetic energy, E_{k}, of the atom equal the energy of the absorbed photon: $E_{\text{k}} = E_{\text{photon}} = \frac{1}{2}m_{\text{He}}v^2$. The values of E_{photon} are calculated in Exercise 7.4b so the atom is accelerated to the speed

$$v = \sqrt{\frac{2E_{\text{photon}}}{m_{\text{He}}}} = \sqrt{\frac{2E_{\text{photon}}}{4.0026\times u}}$$

$$= \sqrt{\frac{2E_{\text{photon}}}{4.0026\times(1.66054\times10^{-27}\ \text{kg})}} = (1.7347\times10^{13}\ \text{m s}^{-1})\times\sqrt{E_{\text{photon}}/\text{J}}$$

We can therefore draw up the following table:

λ	E_{photon}/J	$v/(\text{km s}^{-1})$
(a) 200×10^{-9}	9.93×10^{-19}	17.3
(b) 150×10^{-12}	1.32×10^{-15}	630
(c) 1.00×10^{-2}	1.99×10^{-23}	0.0774

E7.6(b) The total energy emitted in time Δt is $P\Delta t$, where P is the power of the emission. The energy of each emitted photon $E = hc/\lambda$ [7.1]. The total number of photons emitted in an interval Δt is then the total energy divided by the energy per photon.

$$N = \frac{P\Delta t}{E} = \frac{P\Delta t\lambda}{hc}$$

Assuming that de Broglie's relationship applies to each photon, and recognizing that the law of conservation of linear momentum requires that the loss of a photon imparts an equivalent momentum (in the opposite direction) to the spacecraft, the total momentum imparted to the spacecraft in time Δt is

$$p = Np_{\text{photon}} = \frac{Nh}{\lambda}\,[7.16] = \frac{P\Delta t\lambda}{hc} \times \frac{h}{\lambda} = \frac{P\Delta t}{c}$$

Since $p = (mv)_{\text{spacecraft}}$, the final speed of the spacecraft is

$$v = \frac{P\Delta t}{cm_{\text{spacecraft}}} = \frac{(1.50 \times 10^3\ \text{W}) \times (10\ \text{y}) \times (3.1557 \times 10^7\ \text{s y}^{-1})}{(2.9979 \times 10^8\ \text{m s}^{-1}) \times (10.0\ \text{kg})} = \boxed{158\ \text{m s}^{-1}}$$

E7.7(b) The total energy emitted in time Δt is $P\Delta t$ where P is the power of the emission. The energy of each emitted photon is given by $E = hc/\lambda$ [7.1]. The total number of photons emitted in an interval Δt is then the total energy divided by the energy per photon.

$$N = \frac{P\Delta t}{E} = \frac{P\Delta t\lambda}{hc}$$

$$= \frac{(1.00\ \text{s}) \times (700 \times 10^{-9}\ \text{m})}{(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1})} P = (3.52 \times 10^{18}) \times P/\text{W}$$

(a) When $P = 0.10$ W, $N = \boxed{3.52 \times 10^{17}}$.

(b) When $P = 1.0$ W, $N = \boxed{3.52 \times 10^{18}}$.

E7.8(b) $E_k = h\nu - \Phi = \frac{hc}{\lambda} - \Phi\,[7.15]$ and, since $E_k = \frac{1}{2}m_e v^2$, $v = \sqrt{2E_k/m_e}$

$\Phi = 2.09\ \text{eV} = (2.09) \times (1.602 \times 10^{-19}\ \text{J}) = 3.35 \times 10^{-19}\ \text{J}$

(a) For $\lambda = 650$ nm

$$E_k = \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1})}{650 \times 10^{-9}\ \text{m}} - 3.35 \times 10^{-19}\ \text{J} = 3.06 \times 10^{-19}\ \text{J} - 3.35 \times 10^{-19}\ \text{J}$$

Inspection of the above equation reveals that the photon energy of the radiation is less than the work function and we conclude that $\boxed{\text{no electron ejection}}$ occurs.

(b) For $\lambda = 195$ nm

$$E_k = \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1})}{195 \times 10^{-9}\ \text{m}} - 3.35 \times 10^{-19}\ \text{J} = 1.02 \times 10^{-18}\ \text{J} - 3.35 \times 10^{-19}\ \text{J}$$

$$= \boxed{6.84 \times 10^{-19}\ \text{J}}$$

$$v = \sqrt{2 \times (6.84 \times 10^{-19}\ \text{J})/(9.109 \times 10^{-31}\ \text{kg})} = \boxed{1.23\ \text{Mm s}^{-1}}$$

E7.9(b) $\Delta E = h\nu = h/T$ $[T = \text{period} = 1/\nu]$ and $\Delta E_m = N_A \Delta E$

(a) For $T = 2.50$ fs

$$\Delta E = (6.626 \times 10^{-34}\ \text{J s})/(2.50 \times 10^{-15}\ \text{s}) = \boxed{2.65 \times 10^{-19}\ \text{J}}$$

$$\Delta E_m = (6.022 \times 10^{23}\ \text{mol}^{-1}) \times (2.65 \times 10^{-19}\ \text{J}) = \boxed{160\ \text{kJ mol}^{-1}}$$

(b) For $T = 2.21$ fs

$$\Delta E = (6.626\times10^{-34}\ \text{J s})/(2.21\times10^{-15}\ \text{s}) = \boxed{3.00\times10^{-19}\ \text{J}}$$

$$\Delta E_{\text{m}} = (6.022\times10^{23}\ \text{mol}^{-1})\times(3.00\times10^{-19}\ \text{J}) = \boxed{181\ \text{kJ mol}^{-1}}$$

(c) For $T = 1.0$ ms

$$\Delta E = (6.626\times10^{-34}\ \text{J s})/(1.0\times10^{-3}\ \text{s}) = \boxed{6.6\times10^{-31}\ \text{J}}$$

$$\Delta E_{\text{m}} = (6.022\times10^{23}\ \text{mol}^{-1})\times(6.6\times10^{-31}\ \text{J}) = \boxed{4.0\times10^{-10}\ \text{kJ mol}^{-1}}$$

E7.10(b) The de Broglie wavelength is $\lambda = \dfrac{h}{p}$ [7.16]. The kinetic energy acquired by an electron on acceleration through a voltage of $\mathcal{E}$ equals $e\mathcal{E}$. Thus, since $E_{\text{k}} = \dfrac{p^2}{2m_{\text{e}}}$, $p = (2m_{\text{e}}E_{\text{k}})^{1/2} = (2m_{\text{e}}e\mathcal{E})^{1/2}$ and $\lambda = \dfrac{h}{(2me\mathcal{E})^{1/2}}$.

(a) $$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\{2\times(9.109\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})\times(100\ \text{V})\}^{1/2}} = \boxed{123\ \text{pm}}$$

(b) $$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\{2\times(9.109\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})\times(1.0\times10^{3}\ \text{V})\}^{1/2}} = \boxed{39\ \text{pm}}$$

(c) $$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\{2\times(9.109\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})\times(100\times10^{3}\ \text{V})\}^{1/2}} = \boxed{3.88\ \text{pm}}$$

E7.11(b) The normalized wavefunction is $\psi(x) = N\sin(2\pi x/L)$, where N is the normalization constant.

$$\int_0^{2\pi} \psi^*\psi\,\mathrm{d}\varphi = 1\,[7.20\text{a}]$$

$$N^2\int_0^L \sin^2(2\pi x/L)\,\mathrm{d}x = N^2\left\{\frac{x}{2} - \frac{\sin(4\pi x/L)}{8\pi/L}\right\}_{x=0}^{x=L} = \frac{N^2L}{2} = 1$$

$$\boxed{N = \left(\frac{2}{L}\right)^{1/2}}$$

E7.12(b) The normalized wavefunction is $\psi(x) = (2/L)^{1/2}\sin(2\pi x/L)$ so $|\psi(x)|^2 = (2/L)\sin^2(2\pi x/L)$. Thus, the probability of finding the electron in an infinitesimal volume element at $x = L/2$ is

$$|\psi(L/2)|^2\,\mathrm{d}x = (2/L)\sin^2(2\pi L/2L)\,\mathrm{d}x = (2/L)\sin^2(\pi)\,\mathrm{d}x = (2/L)\times0\,\mathrm{d}x = 0$$

The probability of finding the electron in an infinitesimal volume element at the centre of the carbon nanotube equals $\boxed{\text{zero}}$.

E7.13(b) The normalized wavefunction is $\psi = \left(\frac{2}{L}\right)^{1/2} \sin(2\pi x/L)$.

Probability that $L/4 \le x \le L/2 = \int_{L/4}^{L/2} \psi^*\psi \, dx$

$$= \left(\frac{2}{L}\right)\int_{L/4}^{L/2} \sin^2(2\pi x/L)\,dx = \left(\frac{2}{L}\right)\left\{\frac{x}{2} - \frac{\sin(4\pi x/L)}{8\pi/L}\right\}\Bigg|_{x=L/4}^{x=L/2}$$

$$= \left(\frac{2}{L}\right)\left[\left\{\frac{L}{4} - \frac{\sin(4\pi L/2L)}{8\pi/L}\right\} - \left\{\frac{L}{8} - \frac{\sin(4\pi L/4L)}{8\pi/L}\right\}\right]$$

$$= \left\{\frac{1}{2} - \frac{\sin(2\pi)}{4\pi}\right\} - \left\{\frac{1}{4} - \frac{\sin(\pi)}{4\pi}\right\} = \left\{\frac{1}{2} - 0\right\} - \left\{\frac{1}{4} - 0\right\}$$

$$= \boxed{\frac{1}{4}}$$

E7.14(b) The upper sign in the following equations represents the math using the $\hat{A} + i\hat{B}$ operator. The lower sign is for the $\hat{A} - i\hat{B}$ operator. τ is a generalized coordinate.

$$\int \psi_i^* |\hat{A} \pm i\hat{B}| \psi_j \, d\tau = \int \psi_i^* |\hat{A}| \psi_j \, d\tau \pm i\int \psi_i^* |\hat{B}| \psi_j \, d\tau$$

$$= \left\{\int \psi_j^* |\hat{A}| \psi_i \, d\tau\right\}^* \pm i\left\{\int \psi_j^* |\hat{B}| \psi_i \, d\tau\right\}^* \quad \hat{A} \text{ and } \hat{B} \text{ are hermitian [7.33]}$$

$$= \left\{\int \psi_j^* |\hat{A}| \psi_i \, d\tau \mp i\int \psi_j^* |\hat{B}| \psi_i \, d\tau\right\}^* = \left\{\int \psi_j^* |\hat{A} \mp i\hat{B}| \psi_i \, d\tau\right\}^*$$

This shows that the $\hat{A} \pm i\hat{B}$ operators are not hermitian. If they were hermitian, the result would be $\left\{\int \psi_j^* |\hat{A} \pm i\hat{B}| \psi_i \, d\tau\right\}^*$.

E7.15(b) The minimum uncertainty in position is 100 pm. Therefore, since $\Delta x \Delta p \ge \frac{1}{2}\hbar$,

$$\Delta p \ge \frac{\hbar}{2\Delta x} = \frac{1.0546 \times 10^{-34}\,\text{J s}}{2(100 \times 10^{-12}\,\text{m})} = 5.3 \times 10^{-25}\,\text{kg m s}^{-1}$$

$$\Delta v = \frac{\Delta p}{m} = \frac{5.3 \times 10^{-25}\,\text{kg m s}^{-1}}{9.11 \times 10^{-31}\,\text{kg}} = \boxed{5.8 \times 10^{5}\,\text{m s}^{-1}}$$

E7.16(b) $E_{\text{binding}} = E_{\text{photon}} - E_{\text{K}} = h\nu - \frac{1}{2}m_e v^2 = \frac{hc}{\lambda} - \frac{1}{2}m_e v^2$

$$E_{\text{binding}} = \frac{hc}{\lambda} - \frac{1}{2}m_e v^2$$

$$= \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{121 \times 10^{-12}\,\text{m}} - \frac{1}{2}(9.109 \times 10^{-31}\,\text{kg}) \times (5.69 \times 10^{7}\,\text{m s}^{-1})^2$$

$$= (1.67 \times 10^{-16}\,\text{J}) \times \left(\frac{1\,\text{eV}}{1.602 \times 10^{-19}\,\text{J}}\right) = \boxed{1.04\,\text{keV}} \text{ without a relativistic mass correction}$$

Note: The photoelectron is moving at 19.0% of the speed of light. So, in order to calculate a more accurate value of the binding energy, it would be necessary to use the relativistic mass in place of the rest mass.

$$m = \frac{m_e}{(1-(v/c)^2)^{1/2}} = \frac{9.109\times10^{-31}\,\text{kg}}{(1-(5.69\times10^{7}\,\text{m s}^{-1}/2.998\times10^{8}\,\text{m s}^{-1})^2)^{1/2}} = 9.28\times10^{-31}\,\text{kg}$$

$$\begin{aligned}E_{\text{binding}} &= \frac{hc}{\lambda} - \tfrac{1}{2}mv^2\\ &= \frac{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{8}\,\text{m s}^{-1})}{121\times10^{-12}\,\text{m}} - \tfrac{1}{2}(9.28\times10^{-31}\,\text{kg})\times(5.69\times10^{7}\,\text{m s}^{-1})^2\\ &= (1.39\times10^{-16}\,\text{J})\times\left(\frac{1\,\text{eV}}{1.602\times10^{-19}\,\text{J}}\right) = \boxed{0.870\,\text{keV}} \text{ with the relativistic mass correction}\end{aligned}$$

7.17(b) The quantity $[\hat{\Omega}_1,\hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$ [7.41] is referred to as the commutator of the operators $\hat{\Omega}_1$ and $\hat{\Omega}_2$. In obtaining the commutator it is necessary to realize that the operators operate on functions; thus, we find the expression for $[\hat{\Omega}_1,\hat{\Omega}_2]\psi(x) = \hat{\Omega}_1\hat{\Omega}_2\psi(x) - \hat{\Omega}_2\hat{\Omega}_1\psi(x)$.

$$[a,a^{\dagger}]\psi(x) = \left[\frac{\hat{x}+\mathrm{i}\hat{p}}{2^{1/2}},\frac{\hat{x}-\mathrm{i}\hat{p}}{2^{1/2}}\right]\psi(x) = \tfrac{1}{2}[\hat{x}+\mathrm{i}\hat{p},\hat{x}-\mathrm{i}\hat{p}]\psi(x), \quad \text{where} \quad \hat{p} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \quad \text{and} \quad \hat{x} = x\times$$

$$\begin{aligned}&= \tfrac{1}{2}[\hat{x}+\mathrm{i}\hat{p},\hat{x}-\mathrm{i}\hat{p}]\psi(x) = \tfrac{1}{2}\{(\hat{x}+\mathrm{i}\hat{p})(\hat{x}-\mathrm{i}\hat{p}) - (\hat{x}-\mathrm{i}\hat{p})(\hat{x}+\mathrm{i}\hat{p})\}\psi(x)\\ &= \tfrac{1}{2}\left\{(\hat{x}^2+\mathrm{i}\hat{p}\hat{x}-\hat{x}\mathrm{i}\hat{p}-\mathrm{i}^2\hat{p}^2) - (\hat{x}^2-\mathrm{i}\hat{p}\hat{x}+\hat{x}\mathrm{i}\hat{p}-\mathrm{i}^2\hat{p}^2)\right\}\psi(x)\\ &= (\mathrm{i}\hat{p}\hat{x}-\hat{x}\mathrm{i}\hat{p})\psi(x) = \hbar\left(\frac{\mathrm{d}}{\mathrm{d}x}x - x\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi(x) = \hbar\left(\frac{\mathrm{d}}{\mathrm{d}x}x\psi(x) - x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x)\right)\\ &= \hbar\left(\psi(x) + x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) - x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x)\right) = \hbar\psi(x)\end{aligned}$$

Thus, $[a,a^{\dagger}] = \boxed{\hbar}$.

Solutions to problems

Solutions to numerical problems

P7.2 Since $\lambda_{\max}T = \dfrac{hc}{5k}$ by Wien's law, we find the mean of the $\lambda_{\max}T$ values and obtain h from the equation $h = \dfrac{5k}{c}(\lambda_{\max}T)_{\text{mean}}$. We draw up the following table:

θ/°C	1000	1500	2000	2500	3000	3500
T/K	1273	1773	2273	2773	3273	3773
$\lambda_{\max}$/nm	2181	1600	1240	1035	878	763
$\lambda_{\max}T/(10^6\,\text{nm K})$	2.776	2.837	2.819	2.870	2.874	2.879

The mean is 2.84×10^6 nm K with a standard deviation of 0.04×10^6 nm K. Therefore,

$$h = \frac{(5) \times (1.38066 \times 10^{-23}\,\text{J K}^{-1}) \times (2.84 \times 10^{-3}\,\text{m K})}{2.99792 \times 10^{8}\,\text{m s}^{-1}} = \boxed{6.54 \times 10^{-34}\,\text{J s}}$$

COMMENT. Planck's estimate of the constant h in his first paper of 1900 on black-body radiation was 6.55×10^{-27} erg s(1 erg = 10^{-7} J) which is remarkably close to the current value of 6.626×10^{-34} Js and is essentially the same as the value obtained above. Also from his analysis of the experimental data he obtained values of k (the Boltzmann constant), N_A (the Avogadro constant), and e (the fundamental charge). His values of these constants remained the most accurate for almost 20 years.

P7.4 $\psi = \left(\dfrac{2}{L}\right)^{1/2} \sin\left(\dfrac{\pi x}{L}\right)$ and the probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \mathrm{d}x = \frac{2}{L}\int_a^b \sin^2\frac{\pi x}{L}\mathrm{d}x$$

$$= \frac{2}{L}\left(\frac{x}{2} - \frac{L}{4\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_a^b \quad \text{[standard integral, see any mathematics handbook]}$$

$$= \left(\frac{x}{L} - \frac{1}{2\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_a^b = \frac{b-a}{L} - \frac{1}{2\pi}\left(\sin\frac{2\pi b}{L} - \sin\frac{2\pi a}{L}\right)$$

$L = 10.0$ nm

(a) $$P(4.95,5.05) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(5.05)}{10.0} - \sin\frac{(2\pi)\times(4.95)}{10.0}\right) = \boxed{0.020}$$

(b) $$P(1.95,2.05) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(2.05)}{10.0} - \sin\frac{(2\pi)\times(1.95)}{10.0}\right) = \boxed{0.007}$$

(c) $$P(9.90,10.0) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(10.0)}{10.0} - \sin\frac{(2\pi)\times(9.90)}{10.0}\right) = \boxed{7 \times 10^{-6}}$$

(d) $P(5.0,10.0) = \boxed{0.5}$ [by symmetry]

(e) $$P\left(\frac{1}{3}L, \frac{2}{3}L\right) = \frac{1}{3} - \frac{1}{2\pi}\left(\sin\frac{4\pi}{3} - \sin\frac{2\pi}{3}\right) = \boxed{0.61}$$

P7.6 $\psi(x) = N\,\mathrm{e}^{-x^2/2a^2}$

(a) $\displaystyle\int_{-\infty}^{\infty} |\psi(x)|\,\mathrm{d}x = 1$ [normalization condition, 7.20a]

$$N^2 \int_{-\infty}^{\infty} \mathrm{e}^{-x^2/a^2}\mathrm{d}x = 1$$

$$N^2 = \frac{1}{\displaystyle\int_{-\infty}^{\infty} e^{-x^2/a^2}\,dx} = \frac{1}{a\pi^{1/2}} \text{ [standard integral, see any mathematics handbook]}$$

$$\boxed{N = \left(\frac{1}{a\pi^{1/2}}\right)^{1/2}}$$

(b) The probability $P(-a,a)$ that the position is such that $-a \le x \le a$ is

$$P(-a,a) = \int_{-a}^{a} |\psi(x)|\,dx = N^2 \int_{-a}^{a} e^{-x^2/a^2}dx$$

$$= \frac{1}{a\pi^{1/2}} \int_{-a}^{a} e^{-x^2/a^2}dx = \text{erf}(1) = \boxed{0.843}$$

7.8 $$\psi(\phi) = \left(\frac{1}{2\pi}\right)^{1/2} e^{-im\phi} \quad \text{where} \quad m = 0, \pm1, \pm2, \pm3, \ldots$$

The average position (angle) is given by:

$$\langle\phi\rangle = \int \psi^*\phi\psi\,d\tau = \int_0^{2\pi} \left\{\left(\frac{1}{2\pi}\right)^{1/2} e^{-im\phi}\right\}^* \phi \left\{\left(\frac{1}{2\pi}\right)^{1/2} e^{-im\phi}\right\} d\phi$$

$$= \left(\frac{1}{2\pi}\right)\int_0^{2\pi} e^{im\phi}\,\phi\,e^{-im\phi}\,d\phi = \left(\frac{1}{2\pi}\right)\int_0^{2\pi} \phi\,d\phi = \left(\frac{1}{2\pi}\right)\left(\frac{\phi^2}{2}\right)\Bigg|_0^{2\pi}$$

$$= \boxed{\pi}.$$

Note: This result applies to all values of the quantum number m, for it drops out of the calculation.

7.10 The normalized wavefunction is $\psi = (2a)^{1/2}\,e^{-ax}$, where $0 \le x \le \infty$.

The expectation value of the commutator of position and momentum is:

$$\langle[\hat{x},\hat{p}]\rangle = \int_0^{\infty} \psi[\hat{x},\hat{p}]\psi\,dx = \int_0^{\infty} \psi(\hat{x}\hat{p} - \hat{p}\hat{x})\psi\,dx, \quad \text{where} \quad \hat{x} = x\times \quad \text{and} \quad \hat{p} = \frac{\hbar}{i}\frac{d}{dx} \text{ [7.29]}$$

$$= \left(\frac{\hbar}{i}\right)\int_0^{\infty} \psi\left(x\frac{d}{dx} - \frac{d}{dx}x\right)\psi\,dx = \left(\frac{\hbar}{i}\right)\int_0^{\infty} \psi\left(x\frac{d\psi}{dx} - \frac{d(x\psi)}{dx}\right)dx$$

$$= \left(\frac{\hbar}{i}\right)\int_0^{\infty} \psi\left(x\frac{d\psi}{dx} - \psi - x\frac{d\psi}{dx}\right)dx = -\left(\frac{\hbar}{i}\right)\int_0^{\infty} |\psi|^2\,dx$$

$$= -\left(\frac{\hbar}{i}\right) \quad \text{[because } \psi \text{ is normalized to 1]}$$

$= i\hbar$ [this is in agreement with eqn 7.42 and *Justification* 7.6]

Notice that this result only depends on the quantum-mechanical definitions of the position and momentum operators along with the normalization of the wavefunction to 1. The details of how the wavefunction depends on position are irrelevant to this result. Because this commutator is non-zero, position and momentum are **complementary observables** and it is not possible to simultaneously measure both of them with arbitrary precision. This is emphasized by the general form of the Heisenberg uncertainty principle (eqn 7.43), which stipulates that $\Delta x \Delta p \geq \frac{1}{2}|\langle[\hat{x},\hat{p}]\rangle|$.

Solutions to theoretical problems

P7.12 The Planck distribution is $\rho(\lambda,T) = \dfrac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)}$ [7.8].

We look for the value $\lambda = \lambda_{\max}$ at which ρ is a maximum. At this point $\mathrm{d}\rho/\mathrm{d}\lambda = 0$ so we find the derivative and evaluate it at $\lambda = \lambda_{\max}$.

$$\begin{aligned}\frac{\mathrm{d}\rho}{\mathrm{d}\lambda} &= \frac{\mathrm{d}}{\mathrm{d}\lambda}\{8\pi hc\lambda^{-5}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\}\\
&= 8\pi hc\left\{(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\frac{\mathrm{d}\lambda^{-5}}{\mathrm{d}\lambda} + \lambda^{-5}\frac{\mathrm{d}}{\mathrm{d}\lambda}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\right\}\\
&= 8\pi hc\left\{-5\lambda^{-6}(\mathrm{e}^{hc/\lambda kT}-1)^{-1} + \lambda^{-5}(\mathrm{e}^{hc/\lambda kT}-1)^{-2}\left(\frac{hc}{\lambda^2 kT}\right)\mathrm{e}^{hc/\lambda kT}\right\}\\
&= 8\pi hc\lambda^{-7}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\left\{-5\lambda + \left(\frac{hc}{kT}\right)\mathrm{e}^{hc/\lambda kT}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\right\}\end{aligned}$$

Thus, at $\lambda = \lambda_{\max}$

$$-5\lambda_{\max} + \left(\frac{hc}{kT}\right)\mathrm{e}^{hc/\lambda_{\max}kT}(\mathrm{e}^{hc/\lambda_{\max}kT}-1)^{-1} = 0 \quad \text{or} \quad \lambda_{\max} = \left(\frac{hc}{5kT}\right)\mathrm{e}^{hc/\lambda_{\max}kT}(\mathrm{e}^{hc/\lambda_{\max}kT}-1)^{-1}$$

This is a transcendental equation, which can be written in the form

$$x_{\max}\mathrm{e}^{x_{\max}}(\mathrm{e}^{x_{\max}}-1)^{-1} = 5, \quad \text{where} \quad x_{\max} = \frac{hc}{\lambda_{\max}kT}$$

Using the root function or the numeric solver of a scientific calculator to solve for $x_{\max}$, we find $x_{\max} = 4.965$ and

$$\begin{aligned}\lambda_{\max}T &= \frac{hc}{kx_{\max}}\\
&= \frac{(6.626\times10^{-34}\ \mathrm{J\ s^{-1}})\times(2.998\times10^{8}\ \mathrm{m\ s^{-1}})}{4.965\times(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})}\\
&= \boxed{2.898\times10^{-3}\ \mathrm{m\ K}} \quad \text{Prediction of the Planck distribution}\end{aligned}$$

This agrees with Wien's law in that it specifies that $\lambda_{\max}T = \text{constant}$.

P7.14 (a) With a little manipulation, a small-wavelength approximation of the Planck distribution can be derived that has the same form as Wien's formula. First, examine the Planck distribution,

$$\rho_{\text{Planck}} = \frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)},$$

for small-wavelength behaviour. The factor λ^{-5} gets large as λ itself gets small, but the other factor, namely $\frac{1}{\mathrm{e}^{hc/\lambda kT}-1}$, gets small even faster. Focus on that factor, and try to express it in terms of a single decaying exponential (as in Wien's formula), at least in the small-λ limit. Multiplying it by one in the form of $\frac{\mathrm{e}^{-hc/\lambda kT}}{\mathrm{e}^{-hc/\lambda kT}}$, yields $\frac{\mathrm{e}^{-hc/\lambda kT}}{1-\mathrm{e}^{-hc/\lambda kT}}$, where $\mathrm{e}^{-hc/\lambda kT}$ is small, so let us call it ε. The factor, then, becomes $\frac{\varepsilon}{1-\varepsilon}$, which can be expressed as a power series in ε as $\varepsilon(1+\varepsilon\ldots)$. For sufficiently small wavelengths, then, the Planck distribution may be approximated as:

$$\rho_{\text{Planck}} \approx \frac{8\pi hc\varepsilon}{\lambda^5} = \frac{8\pi hc\mathrm{e}^{-hc/\lambda kT}}{\lambda^5}$$

This has the same form as Wien's formula:

$$\rho_{\text{Wien}} = \frac{a}{\lambda^5}\mathrm{e}^{-b/\lambda kT}$$

Comparing the two formulas gives the values of the Wien constants: $a = \boxed{8\pi hc}$ and $b = \boxed{hc}$

(b) The wavelength at which the Planck distribution, $\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)}$ [7.8], is a maximum is found by setting the derivative of the distribution function with respect to wavelength equal to zero and solving the resulting transcendental equation with the numeric solver of a scientific calculator (see Problem 7.12). This gives

$$\lambda_{\max}T = \frac{hc}{4.965\,k} = 2.898\times10^{-3}\,\text{m K} \quad \text{Prediction of the Planck distribution}$$

Following the same procedure with the Wien distribution gives a very similar result.

$$\frac{\mathrm{d}\rho_{\text{Wein}}}{\mathrm{d}\lambda} = \frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\frac{8\pi hc}{\lambda^5}\mathrm{e}^{-hc/\lambda kT}\right) = 8\pi hc\left\{-\frac{5}{\lambda^6}\mathrm{e}^{-hc/\lambda kT} + \left(\frac{1}{\lambda^5}\right)\left(\frac{hc}{\lambda^2 kT}\right)\mathrm{e}^{-hc/\lambda kT}\right\}$$

$$= 8\pi hc\lambda^{-7}\mathrm{e}^{-hc/\lambda kT}\left\{-5\lambda + \left(\frac{hc}{kT}\right)\right\}$$

This derivative equals zero when the distribution is a maximum at $\lambda = \lambda_{\max}$ and inspection of the factors reveals that this occurs when

$$-5\lambda_{\max} + \left(\frac{hc}{kT}\right) = 0 \quad \text{or} \quad \lambda_{\max}T = \frac{hc}{5k} \quad \text{Prediction of the Wien distribution}$$

Thus, the maximum of the Wien distribution agrees well with that of the Planck distribution. The only difference being a factor of 1/4.965 in the expression for $\lambda_{\max}T$ in the Planck distribution and a factor of 1/5 for the Wien distribution.

The Stefan–Boltzmann law gives the energy density $\mathcal{E}$ as a function of temperature. According to the Planck distribution (see Problem 7.13), the energy density of black-body radiation is

$$\mathcal{E}_{\text{Planck}} = \int_0^{\infty} \rho_{\text{Planck}}(\lambda)\text{d}\lambda = \left(\frac{4}{c}\right)\sigma T^4$$

where $\sigma = \dfrac{2\pi^5 k^4}{15h^3c^2} = 5.671 \times 10^{-8}\ \text{kg s}^{-3}\ \text{K}^{-4}$ is the Stefan–Boltzmann constant

The energy density of the Wien distribution is

$$\mathcal{E}_{\text{Wien}} = \int_0^{\infty} \rho_{\text{Wien}}(\lambda)\ \text{d}\lambda = 8\pi hc \int_0^{\infty} \frac{\text{e}^{-hc/\lambda kT}\text{d}\lambda}{\lambda^5}$$

Let $x = \dfrac{hc}{\lambda kT}$. Then, $\text{d}x = -\dfrac{hc}{\lambda^2 kT}\text{d}\lambda$ or $\text{d}\lambda = -\dfrac{\lambda^2 kT}{hc}\text{d}x$

$$\begin{aligned}\mathcal{E}_{\text{Wien}} &= 8\pi kT \int_0^{\infty} \frac{\text{e}^{-x}\lambda^2\text{d}x}{\lambda^5} = 8\pi kT \int_0^{\infty} \frac{\text{e}^{-x}\text{d}x}{\lambda^3} = 8\pi kT\left(\frac{kT}{hc}\right)^3 \int_0^{\infty} x^3\text{e}^{-x}\text{d}x \\ &= 8\pi kT\left(\frac{kT}{hc}\right)^3 (6) \quad \text{[standard integral]} \\ &= \boxed{\left(\frac{4}{c}\right)\sigma_{\text{Wien}}T^4}, \quad \text{where} \quad \sigma_{\text{Wien}} = \frac{12\pi k^4}{h^3c^2} = 5.239 \times 10^{-8}\ \text{kg s}^{-3}\ \text{K}^{-4}\end{aligned}$$

Comparing the energy densities of the Planck and Wien distributions, we see that both predict that the energy density is proportional to T^4. However, the Wien distribution predicts a constant of proportionality that is low by about 8%.

P7.16 In each case the normalization constant $N^{-2} = \int |\psi|^2\text{d}\tau$ [7.19] must be evaluated by analytically determining the integral over the whole space of the wavefunction. The normalization integrals are best evaluated using the spherical coordinates (r,θ,ϕ) for which $0 \le r \le \infty$, $0 \le \theta \le \pi$, and $0 \le \phi \le 2\pi$. It is helpful to recognize that, when a wavefunction has the separation of variables form $\psi(r,\theta,\phi) = R(r) \times \Theta(\theta) \times \Phi(\phi)$, the integral over the space of all variables is

$$\begin{aligned}N^{-2} &= \int |\psi|^2\ \text{d}\tau = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} |\psi|^2 r^2 \sin\theta\ \text{d}r\ \text{d}\theta\ \text{d}\phi\ [\text{note that } \text{d}\tau = r^2\sin\theta\ \text{d}r\ \text{d}\theta\ \text{d}\phi] \\ &= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} r^2 \times (R(r) \times \Theta(\theta) \times \Phi(\phi))^2 \sin\theta\ \text{d}r\ \text{d}\theta\ \text{d}\phi \\ &= \int_{r=0}^{\infty} r^2 \times R(r)^2\text{d}r \times \int_{\theta=0}^{\pi} \sin(\theta) \times \Theta(\theta)^2\text{d}\theta \times \int_{\phi=0}^{2\pi} \Phi(\phi)^2\text{d}\phi\end{aligned}$$

In the special case (i) for which $\Theta(\theta) = 1$ and $\Phi(\phi) = 1$:

$$\int_{\theta=0}^{\pi} \sin(\theta) \times \Theta(\theta)^2\text{d}\theta \times \int_{\phi=0}^{2\pi} \Phi(\phi)^2\text{d}\phi = \int_{\theta=0}^{\pi} \sin(\theta)\text{d}\theta \times \int_{\phi=0}^{2\pi} \text{d}\phi = [-\cos\theta]_{\theta=0}^{\pi} \times [\phi]_{\phi=0}^{2\pi} = 4\pi$$

and the normalization integral is

$$N^{-2} = 4\pi\int_{r=0}^{\infty} r^2 \times R(r)^2\mathrm{d}r$$

In the special case (ii) for which $\Theta(\theta) = \sin\theta$ and $\Phi(\phi) = \cos\phi$:

$$\int_{\theta=0}^{\pi} \sin(\theta)\times\Theta(\theta)^2\mathrm{d}\theta \times \int_{\phi=0}^{2\pi}\Phi(\phi)^2\mathrm{d}\phi = \int_{\theta=0}^{\pi}\sin^3(\theta)\mathrm{d}\theta \times \int_{\phi=0}^{2\pi}\cos^2(\phi)\mathrm{d}\phi$$

$$= \left[-\cos\theta + \tfrac{1}{3}\cos^3\theta\right]_{\theta=0}^{\pi} \times \left[\tfrac{\phi}{2} + \tfrac{1}{4}\sin 2\phi\right]_{\phi=0}^{2\pi} = \tfrac{4}{3}\pi$$

and the normalization integral is

$$N^{-2} = \tfrac{4}{3}\pi\int_{r=0}^{\infty} r^2 \times R(r)^2\mathrm{d}r$$

(a) (i) The unnormalized wavefunction is $\psi = \left(2 - \dfrac{r}{a_0}\right)\mathrm{e}^{-r/a_0}$ and $\psi^2 = \left(2 - \dfrac{r}{a_0}\right)^2\mathrm{e}^{-2r/a_0}$

$$N^{-2} = 4\pi\int_{r=0}^{\infty} r^2 \times R(r)^2\mathrm{d}r$$

$$= 4\pi\int_{r=0}^{\infty} r^2 \times \left\{\left(2 - \frac{r}{a_0}\right)\mathrm{e}^{-r/a_0}\right\}^2 \mathrm{d}r$$

$$= 4\pi a_0^3\int_{\chi=0}^{\infty} \chi^2 \times \{(2-\chi)\mathrm{e}^{-\chi}\}^2\mathrm{d}\chi, \quad \text{where} \quad \chi = r/a_0$$

$$= 4\pi a_0^3\int_{\chi=0}^{\infty}\{4\chi^2 - 4\chi^3 + \chi^4\}\mathrm{e}^{-2\chi}\mathrm{d}\chi\left[\text{use the standard integral} \int_0^{\infty}\chi^n\mathrm{e}^{-a\chi}\mathrm{d}\chi = n!/a^{n+1}\right]$$

$$= 4\pi a_0^3\{4\times 2!/2^{2+1} - 4\times 3!/2^{3+1} + 4!/2^{4+1}\} = \pi a_0^3$$

Hence, $\boxed{N = (\pi a_0^3)^{-1/2}}$ and the normalized wavefunction is $\psi = \left(\dfrac{1}{\pi a_0^3}\right)^{1/2}\left(2 - \dfrac{r}{a_0}\right)\mathrm{e}^{-r/a_0}$.

(ii) The unnormalized wavefunction is $\psi = r\sin\theta\cos\varphi\ \mathrm{e}^{-r/2a_0}$ and $\psi^2 = r^2\sin^2\theta\cos^2\varphi\,\mathrm{e}^{-r/a_0}$.

$$N^{-2} = \tfrac{4}{3}\pi\int_{r=0}^{\infty} r^2 \times R(r)^2\mathrm{d}r$$

$$= \tfrac{4}{3}\pi\int_{r=0}^{\infty} r^2 \times \{r\,\mathrm{e}^{-r/2a_0}\}^2\mathrm{d}r$$

$$= \tfrac{4}{3}\pi a_0^5\int_{\chi=0}^{\infty}\chi^4\mathrm{e}^{-\chi}\mathrm{d}\chi, \quad \text{where} \quad \chi = r/a_0$$

$$= (\tfrac{4}{3}\pi a_0^5)\times(4!) \quad \left[\text{use the standard integral} \int_0^{\infty}\chi^n\mathrm{e}^{-a\chi}\mathrm{d}\chi = n!/a^{n+1}\right] = 32\pi a_0^5$$

Hence, $\boxed{N = (32\pi a_0^5)^{-1/2}}$ and the normalized wavefunction is $\psi = \left(\dfrac{1}{32\pi a_0^5}\right)^{1/2} r\sin\theta\cos\varphi\,\mathrm{e}^{-r/2a_0}$.

(b) Since normalization constants do not affect orthogonality, we use the unnormalized wavefunctions to examine the integral $\int\psi_1\psi_2\mathrm{d}\tau$. The wavefunctions are orthogonal if the integral proves to equal zero.

$$\int\psi_1\psi_2\mathrm{d}\tau = \int\left\{\left(2-\frac{r}{a_o}\right)\mathrm{e}^{-r/a_o}\right\}\{r\sin\theta\,\cos\phi\,\mathrm{e}^{-r/2a_o}\}\mathrm{d}\tau$$

$$= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left\{\left(2-\frac{r}{a_o}\right)\mathrm{e}^{-r/a_o}\right\}\{r\sin\theta\,\cos\phi\,\mathrm{e}^{-r/2a_o}\}r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= \int_{r=0}^{\infty}\left\{\left(2r^3-\frac{r^4}{a_o}\right)\mathrm{e}^{-3r/2a_o}\right\}\mathrm{d}r \times \int_{\theta=0}^{\pi}\sin^2\theta\,\mathrm{d}\theta \times \int_{\phi=0}^{2\pi}\cos\phi\,\mathrm{d}\phi$$

The integral on the far right equals zero: $\displaystyle\int_{\phi=0}^{2\pi}\cos\phi\,\mathrm{d}\phi = \sin\phi\Big|_0^{2\pi} = \sin(2\pi)-\sin(0) = 0-0 = 0$

Hence, $\int\psi_1\psi_2\mathrm{d}\tau = 0$ and we conclude that the wavefunctions are orthogonal.

P7.18 Operate on each function f with $\hat{\imath}$ (the inversion operator, which has the effect of making the replacement $x \to -x$). If the result of the operation is f multiplied by a constant, f is an eigenfunction of $\hat{\imath}$ and the constant is the eigenvalue [7.28a, 7.28b, and 7.28c].

(a) $f = x^3 - kx$

$\hat{\imath}(x^3-kx) = -x^3 + kx = -f$

$\boxed{\text{Yes}}$, f is an eigenfunction with eigenvalue $\boxed{-1}$.

(b) $f = \cos kx$

$\hat{\imath}\cos kx = \cos(-kx) = \cos kx = f$

$\boxed{\text{Yes}}$, f is an eigenfunction with eigenvalue $\boxed{+1}$.

(c) $f = x^2 + 3x - 1$

$\hat{\imath}(x^2+3x-1) = x^2 - 3x - 1 \neq \text{constant} \times f$

$\boxed{\text{No}}$, f is not an eigenfunction of $\hat{\imath}$.

P7.20 The quantum-mechanical operators are constructed by first writing the classical expression for the observable and then making operator substitutions for position and momentum. The operators for the x components of position and momentum are

$$\hat{x} = x\times \quad\text{and}\quad \hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\ [7.29]$$

The operator for p_x^2 is

$$\hat{p}_x^2 = \hat{p}_x\hat{p}_x = \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right) = -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2} \quad \text{for one-dimensional systems}$$

$$= -\hbar^2\left(\frac{\partial^2}{\partial x^2}\right)_{y,z} \quad \text{for three-dimensional systems}$$

(a) Kinetic energy in one dimension:

$$\hat{E}_\mathrm{k} = \frac{1}{2m}\hat{p}_x^2 = \boxed{-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}}$$

Kinetic energy in three dimensions:

$$\hat{E}_\mathrm{k} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) = -\frac{\hbar^2}{2m}\left(\left(\frac{\partial^2}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2}{\partial z^2}\right)_{x,y}\right)$$

$$= \boxed{-\frac{\hbar^2}{2m}\nabla^2}, \quad \text{where} \quad \nabla^2 = \left(\frac{\partial^2}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2}{\partial z^2}\right)_{x,y} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

(b) The inverse separation, $1/x$:

$$\frac{\hat{1}}{x} = \boxed{\frac{1}{x}\times}$$

The inverse separation in three dimensions is determined by the vector magnitude of the position vector $\vec{r} = x\vec{\mathbf{i}} + y\vec{\mathbf{j}} + z\vec{\mathbf{k}}$:

$$\frac{\hat{1}}{r} = \boxed{\frac{1}{\{x^2+y^2+z^2\}^{1/2}}}$$

(c) The electric dipole moment operator for J point charges Q_J at the vector positions $\vec{r}_\mathrm{J}$ is

$$\hat{\mu}_x\vec{\mathbf{i}} + \hat{\mu}_y\vec{\mathbf{j}} + \hat{\mu}_z\vec{\mathbf{k}} = \sum_\mathrm{J} Q_\mathrm{J}x_\mathrm{J}\vec{\mathbf{i}} + \sum_\mathrm{J} Q_\mathrm{J}y_\mathrm{J}\vec{\mathbf{j}} + \sum_\mathrm{J} Q_\mathrm{J}z_\mathrm{J}\vec{\mathbf{k}}$$

The magnitude of the electric dipole moment, μ, is

$$\mu = \{\mu_x^2 + \mu_y^2 + \mu_z^2\}^{1/2} = \left\{\left(\sum_\mathrm{J} Q_\mathrm{J}x_\mathrm{J}\right)^2 + \left(\sum_\mathrm{J} Q_\mathrm{J}y_\mathrm{J}\right)^2 + \left(\sum_\mathrm{J} Q_\mathrm{J}z_\mathrm{J}\right)^2\right\}^{1/2}$$

(d) The root mean square deviation of position in one dimension is

$$\Delta x = \boxed{\{\langle x^2\rangle - \langle x\rangle^2\}^{1/2}} \; [7.39\mathrm{b}]$$

The root mean square deviation of momentum in one dimension is

$$\Delta p_x = \left\{\left\langle\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2\right\rangle - \left\langle\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right\rangle^2\right\}^{1/2} [7.39\mathrm{b}] = \boxed{\frac{\hbar}{\mathrm{i}}\left\{\left\langle\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right\rangle - \left\langle\frac{\mathrm{d}}{\mathrm{d}x}\right\rangle^2\right\}^{1/2}}$$

P7.22 The wavefunction $\psi = (\cos\chi)e^{+ikx} + (\sin\chi)e^{-ikx} = c_1e^{+ikx} + c_2e^{-ikx}$ is a superposition of the functions e^{+ikx} and e^{-ikx}. We first demonstrate that the functions e^{+ikx} and e^{-ikx} are eigenfunctions of the linear momentum operator, $\hat{p}_x = \dfrac{\hbar}{i}\dfrac{d}{dx}$ [7.29], that have the eigenvalues $+k\hbar$ and $-k\hbar$, respectively.

$$\hat{p}_x e^{+ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{+ikx} = \left(\frac{\hbar}{i}\right) \times (ik)e^{+ikx} = +k\hbar e^{+ikx}$$

$$\hat{p}_x e^{-ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{-ikx} = \left(\frac{\hbar}{i}\right) \times (-ik)e^{-ikx} = -k\hbar e^{-ikx}$$

Because these functions are eigenfunctions of the momentum operator and the system wavefunction is a superposition of them, by the principle of linear superposition of eigenfunctions (Section 7.5(e), *Justification* 7.5) the probability of measuring a particular momentum eigenvalue in a series of observations is proportional to the square modulus ($|c_k|^2$) of the corresponding coefficient in the superposition expression of ψ.

(a) The probability of observing the linear momentum $+k\hbar$ is $|c_1|^2 = \boxed{\cos^2\chi}$

(b) The probability of observing the linear momentum $-k\hbar$ is $|c_2|^2 = \boxed{\sin^2\chi}$

(c) $|c_1|^2 = 0.90$ and, taking c_1 to be positive, $c_1 = 0.95$.

Since the sum of the probabilities must equal 1, $|c_2|^2 = 1 - |c_1|^2 = 0.10$ and, therefore, $c_2 = \pm 0.32$.

Hence, the wavefunction is $\boxed{\psi = 0.95\,e^{ikx} \pm 0.32\,e^{-ikx}}$

P7.24 (a) The function e^{+ikx} is an eigenfunction of the linear momentum operator, $\hat{p}_x = \dfrac{\hbar}{i}\dfrac{d}{dx}$ [7.29]. It has the eigenvalues $+k\hbar$:

$$\hat{p}e^{+ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{+ikx} = \left(\frac{\hbar}{i}\right) \times (ik)e^{+ikx} = +k\hbar e^{+ikx}$$

Consequently, the particle has the linear momentum $\boxed{+k\hbar}$

(b) The wavefunction $\psi = N\cos kx$ is not an eigenfunction of the linear momentum operator so we find the expectation value for linear momentum with eqn 7.37.

$$\langle p_x\rangle = \int_{-\infty}^{\infty} \psi^*\hat{p}_x\psi\,dx\ [7.37] = N^2\int_{-\infty}^{\infty} \cos kx\left(\frac{\hbar}{i}\frac{d}{dx}\right)\cos kx\,dx$$

$$= N^2\left(\frac{\hbar}{i}\right)\int_{-\infty}^{\infty} \cos kx\left(\frac{d}{dx}\right)\cos kx\,dx = -kN^2\left(\frac{\hbar}{i}\right)\int_{-\infty}^{\infty} \cos kx \sin kx\,dx$$

$$= -kN^2\left(\frac{\hbar}{i}\right)\lim_{\chi\to\infty}\left[\frac{\sin^2 kx}{2k}\right]_{x=-\chi}^{x=\chi} \quad \text{[standard integral]}$$

$$= -kN^2\left(\frac{\hbar}{i}\right)\lim_{\chi\to\infty}\left[\frac{\sin^2(k\chi)}{2k} - \frac{\sin^2(-k\chi)}{2k}\right] = -kN^2\left(\frac{\hbar}{i}\right)\lim_{\chi\to\infty}\left[\frac{\sin^2(k\chi)}{2k} - \frac{\sin^2(k\chi)}{2k}\right] = \boxed{0}$$

(c) $\psi = N\mathrm{e}^{-ax^2}$

$$\frac{\mathrm{d}}{\mathrm{d}x}\psi = N\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{-ax^2} = -2aNx\mathrm{e}^{-ax^2} = -2ax\psi$$

The wavefunction is not an eigenfunction of the linear momentum operator, so we find the expectation value for linear momentum with eqn 7.37.

$$\langle p_x\rangle = \int_{-\infty}^{\infty}\psi^*\hat{p}_x\psi\mathrm{d}x\ [7.37] = N^2\int_{-\infty}^{\infty}\mathrm{e}^{-ax^2}\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\mathrm{e}^{-ax^2}\mathrm{d}x$$

$$= -2aN^2\left(\frac{\hbar}{\mathrm{i}}\right)\int_{-\infty}^{\infty}x\mathrm{e}^{-2ax^2}\mathrm{d}x$$

The integrand of the above integral is an odd function so, when it is integrated around its centre of symmetry at $x = 0$, the integral equals zero. Thus, $\langle p_x\rangle = \boxed{0}$

P7.26 The normalized ground-state hydrogenic atom (a one-electron atom of atomic number Z) is a generalization of the wavefunction of text Example 7.4:

$$\psi(r) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\mathrm{e}^{-Zr/a_0}$$

The expectation values are best evaluated using the spherical coordinates (r,θ,ϕ) for which $0 \le r \le \infty$, $0 \le \theta \le \pi$, and $0 \le \phi \le 2\pi$. It is helpful to recognize that, when a wavefunction has the separation of variables form $\psi(r,\theta,\phi) = R(r) \times \Theta(\theta) \times \Phi(\phi)$, the expectation integral of the function $f(r)$ over the space of all variables is

$$\langle f(r)\rangle = \int f(r)\,|\psi|^2\,\mathrm{d}\tau$$

$$= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} f(r)\,|\psi|^2\,r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \quad [\text{note that } \mathrm{d}\tau = r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi]$$

$$= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} r^2 f(r) \times (R(r) \times \Theta(\theta) \times \Phi(\phi))^2 \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= \int_{r=0}^{\infty} r^2 f(r) \times R(r)^2\mathrm{d}r \times \int_{\theta=0}^{\pi}\sin(\theta) \times \Theta(\theta)^2\mathrm{d}\theta \times \int_{\phi=0}^{2\pi}\Phi(\phi)^2\mathrm{d}\phi$$

In the special case of the ground state of the hydrogenic atom for which $\Theta(\theta) = 1$, $\Phi(\phi) = 1$ and $R(r) = \psi(r)$:

$$\int_{\theta=0}^{\pi}\sin(\theta) \times \Theta(\theta)^2\mathrm{d}\theta \times \int_{\phi=0}^{2\pi}\Phi(\phi)^2\mathrm{d}\phi = \int_{\theta=0}^{\pi}\sin(\theta)\mathrm{d}\theta \times \int_{\phi=0}^{2\pi}\mathrm{d}\phi$$

$$= \left[-\cos\theta\right]_{\theta=0}^{\pi} \times \left[\phi\right]_{\phi=0}^{2\pi}$$

$$= 4\pi$$

and the expectation integral of $f(r)$ is

$$\langle f(r)\rangle = 4\pi\int_{r=0}^{\infty} r^2 f(r)\times R(r)^2\,\mathrm{d}r = 4\pi\int_{r=0}^{\infty} r^2 f(r)\times \psi(r)^2\,\mathrm{d}r$$

(a) The Coulomb potential energy of interaction between the hydrogenic electron and the nucleus of charge $+Ze$ is $V(r) = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$. The mean potential energy of the interaction is given by the expectation value of $V(r)$.

$$\begin{aligned}
\langle V\rangle &= 4\pi\int_{r=0}^{\infty} r^2 V(r)\times\psi(r)^2\,\mathrm{d}r \\
&= 4\pi\int_{r=0}^{\infty} r^2\times\left(-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\times\left\{\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\mathrm{e}^{-Zr/a_0}\right\}^2\mathrm{d}r \\
&= \left(-\frac{Z^4e^2}{\pi\varepsilon_0 a_0}\right)\int_{\chi=0}^{\infty}\chi\mathrm{e}^{-2Z\chi}\,\mathrm{d}\chi\left[\chi = r/a_0;\text{ use the standard integral }\int_0^{\infty}\chi^n\mathrm{e}^{-a\chi}\,\mathrm{d}\chi = n!/a^{n+1}\right] \\
&= \left(-\frac{Z^4e^2}{\pi\varepsilon_0 a_0}\right)\times\left(\frac{1}{4Z^2}\right) = \boxed{-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}}
\end{aligned}$$

(b) The kinetic energy operator for the hydrogenic electron is the sum of the kinetic energy operators (see eqn 7.31) in the x, y, and z directions.

$$\hat{E}_\mathrm{k} = \hat{E}_{\mathrm{k},x} + \hat{E}_{\mathrm{k},y} + \hat{E}_{\mathrm{k},z} = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla^2,\quad\text{where}\quad \nabla^2 = \left(\frac{\partial^2}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2}{\partial z^2}\right)_{x,y}$$

The operator ∇^2 is called the Laplacian and, when written in spherical polar coordinates, it has the form (see a mathematics textbook):

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Luckily, when the Laplacian operates on a function of r alone, the last two terms vanish because

$$\frac{\partial\psi(r)}{\partial\theta} = 0\quad\text{and}\quad\frac{\partial\psi(r)}{\partial\phi} = 0$$

Consequently,

$$\begin{aligned}
\nabla^2\psi(r) &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(r) = \frac{1}{r^2}\left(2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2}\right)\psi(r) = \frac{1}{r}\left(2\frac{\partial}{\partial r} + r\frac{\partial^2}{\partial r^2}\right)\psi(r) \\
&= \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\frac{1}{r}\left(2\frac{\partial}{\partial r} + r\frac{\partial^2}{\partial r^2}\right)\mathrm{e}^{-Zr/a_0} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\frac{1}{r}\left(2\frac{\partial\mathrm{e}^{-Zr/a_0}}{\partial r} + r\frac{\partial^2\mathrm{e}^{-Zr/a_0}}{\partial r^2}\right) \\
&= \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\frac{1}{r}\left(\frac{-2Z}{a_0}\mathrm{e}^{-Zr/a_0} + \frac{Z^2}{a_0^2}r\mathrm{e}^{-Zr/a_0}\right) = \left(\frac{Z^5}{\pi a_0^5}\right)^{1/2}\frac{1}{r}\left(-2\mathrm{e}^{-Zr/a_0} + \frac{Z}{a_0}r\mathrm{e}^{-Zr/a_0}\right)
\end{aligned}$$

The above relationship is useful when evaluating the expectation value of E_k.

$$\langle E_k\rangle = 4\pi\int_{r=0}^{\infty} r^2\psi(r)\hat{E}_k\psi(r)\mathrm{d}r = 4\pi\int_{r=0}^{\infty} r^2\psi(r)\times\left(-\frac{\hbar^2}{2m_e}\nabla^2\right)\times\psi(r)\mathrm{d}r$$

$$=\left(-\frac{2\pi\hbar^2}{m_e}\right)\int_{r=0}^{\infty} r^2\left\{\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\mathrm{e}^{-Zr/a_0}\right\}\times\left\{\left(\frac{Z^5}{\pi a_0^5}\right)^{1/2}\frac{1}{r}\left(-2\mathrm{e}^{-Zr/a_0}+\frac{Z}{a_0}r\mathrm{e}^{-Zr/a_0}\right)\right\}\mathrm{d}r$$

$$=\left(-\frac{2\hbar^2Z^4}{m_e a_0^4}\right)\int_{r=0}^{\infty}\left(-2r\mathrm{e}^{-2Zr/a_0}+\frac{Z}{a_0}r^2\mathrm{e}^{-2Zr/a_0}\right)\mathrm{d}r\ [\text{substitute } \chi = r/a_0]$$

$$=\left(-\frac{2\hbar^2Z^4}{m_e a_0^2}\right)\int_{\chi=0}^{\infty}(-2\chi\mathrm{e}^{-2Z\chi}+Z\chi^2\mathrm{e}^{-2Z\chi})\mathrm{d}\chi\left[\text{use the standard integral }\int_0^{\infty}\chi^n\mathrm{e}^{-a\chi}\mathrm{d}\chi = n!/a^{n+1}\right]$$

$$=\left(-\frac{2\hbar^2Z^4}{m_e a_0^2}\right)\times\left(-\frac{2}{4Z^2}+\frac{1}{4Z^2}\right)=\boxed{\frac{\hbar^2Z^2}{2m_e a_0^2}}$$

P7.28 For the hermitian operator $\hat{\Omega}$: $\langle\Omega^2\rangle = \int\psi^*\hat{\Omega}^2\psi\mathrm{d}\tau = \int\psi^*\hat{\Omega}(\hat{\Omega}\psi)\mathrm{d}\tau = \{\int(\hat{\Omega}\psi)^*\hat{\Omega}\psi\mathrm{d}\tau\}^*$ [7.33]

The integrand on the far right is a function times its complex conjugate, which must always be a real, positive number. When this type of integrand is integrated over real space, the result is always a real, positive number. Thus, the expectation value of the square of a hermitian operator is always positive.

Solutions to applications: nanoscience, environmental science, and astrophysics

P7.30 The wavelength $\lambda_{\max}$ at which the spectral distribution of the sun is a maximum is nicely estimated with Wien's law (see Problem 7.14)

$$\lambda_{\max} = \frac{hc}{5kT}\ [\text{Wien's law}] = \frac{(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{8}\ \mathrm{m\ s^{-1}})}{5\times(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(5800\ \mathrm{K})}$$

$$= 4.96\times10^{-7}\ \mathrm{m} = \boxed{49\bar{6}\ \text{nm, blue-green}}$$

P7.32 We begin by reviewing the Stefan–Boltzmann law, derived in Problem 7.13, that relates the total energy density $\mathcal{E}$ of black-body radiation to the temperature T of the body:

$$\mathcal{E} = \int_0^{\infty}\rho(\lambda)\mathrm{d}\lambda = 8\pi hc\int_0^{\infty}\frac{\mathrm{d}\lambda}{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)}\ [7.8] = \left(\frac{4}{c}\right)\sigma T^4$$

where $\sigma = \dfrac{2\pi^5k^4}{15h^3c^2} = 5.671\times10^{-8}\ \mathrm{W\ m^{-2}\ K^{-4}}$ is the Stefan–Boltzmann constant.

The power emitted by a region of surface divided by the area of the surface is called the excitance M and it can be shown (though it is difficult) that according to the Stefan–Boltzmann law: $M = \frac{c}{4}\mathcal{E} = \sigma T^4$.

Let I_{solar} ($= 343\ \text{W m}^{-2}$) be the solar energy flux at the top of the Earth's atmosphere and let a ($= 0.30$) be the albedo, the fraction of the solar flux that is reflected back into space by the Earth or the atmosphere. The solar energy absorbed by the Earth is $(1 - a)I_{\text{solar}}$. The radiation energy emitted by the Earth is the Earth's excitance. Since the average temperature of the Earth changes but little over tens of thousands of years or more, we surmise that there is a steady-state balance between the energy absorbed by the Earth and the radiation energy emitted (and lost into space) by the Earth. That is

$$(1 - a)I_{\text{solar}} = \sigma T^4$$

$$T = \left(\frac{(1-a)I_{\text{solar}}}{\sigma}\right)^{1/4} = \left(\frac{(1-0.30)(343\ \text{W m}^{-2})}{5.671\times 10^{-8}\ \text{W m}^{-2}\ \text{K}^{-4}}\right)^{1/4} = \boxed{25\bar{5}\ \text{K or } 1\bar{8}\,^\circ\text{C}}$$

Wien's law, which is derived in Problem 7.12, relates the temperature to the wavelength of the most intense radiation

$$\lambda_{\max} = \frac{hc}{5kT} = \frac{(6.626\times 10^{-34}\ \text{J s})\times(2.998\times 10^{8}\ \text{m s}^{-1})}{5\times(1.381\times 10^{-23}\ \text{J K}^{-1})\times(25\bar{5}\ \text{K})} = \boxed{11\ \mu\text{m}}$$

P7.34 See Problem 7.27 for the free-particle superposition of $\cos(nx)$ functions where the quantum number n can take on the values 1, 2, 3, … , etc. The particle of the current problem, an electron, is not entirely free. It is trapped in a nanotube of length L. The diameter of the nanotube is about 1 nm and we will take the length to be about 1 μm. Since the diameter is very much smaller than the length, the problem is conveniently approximated as involving motion in one dimension only. That is, there is a 100% probability that the electron is between $x = 0$ and $x = L$, where the coordinate x starts at one end of the nanotube.

It is possible to construct a superposition of cosine functions but it is somewhat more convenient to choose the option of superpositioning sine functions. The two functions differ by a phase, $\sin\theta = \cos(\theta - \pi/2)$, and the choice of sine function allows us to satisfy the boundary conditions on the trapped electron without the necessity of incorporating a non-zero phase. The wavefunction of the trapped electron must equal zero at the two boundaries so we guess that acceptable wavefunctions have the form $N\times\sin(ax)$, where a is a constant that is determined by the boundary conditions and N is a constant determined by the normalization of the wavefunction to a probability of 1 within the nanotube. Since $\sin(0) = 0$, the state $N\times\sin(ax)$ satisfies the boundary condition at $x = 0$. The function will satisfy the boundary condition at the other end of the nanotube provided that $\sin(aL) = 0$ and this equality is satisfied provided that $a = n\pi/L$, where $n = 1, 2, 3, \ldots$ The quantum number n appears, as always, because of the restrictions of boundary conditions! The normalization constant is

$$N^{-2} = \int_0^L \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \left[\frac{x}{2} - \frac{L}{4n\pi}\sin\left(\frac{2n\pi x}{L}\right)\right]_0^L = \frac{L}{2}$$

$$N = \left(\frac{2}{L}\right)^{1/2}$$

Thus, the normalized wavefunctions are $\psi_n(x) = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)$, where $n = 1, 2, 3, \ldots$

(These wavefunction will be studied extensively in Section 8.1: A particle in a box.)

It is well worth the time to examine these wavefunctions so we have developed the following Mathcad worksheet to show that they are normalized and that wavefunctions of different quantum numbers are orthogonal. Useful expectation values are also reported.

$$\psi(n,x,L) := \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\cdot\pi\cdot x}{L}\right)$$

Normality check: $\int_0^L \psi(2,x,L)^2 dx = 1$

Orthogonality check: $\int_0^L \psi(2,x,L)\cdot\psi(5,x,L) dx = 0$

Expectation of x: $\int_0^L x\cdot\psi(n,x,L)^2 dx \rightarrow \frac{L\cdot\sin(\pi\cdot n)^2 + \pi^2\cdot L\cdot n^2 - \pi\cdot L\cdot n\cdot\sin(2\cdot\pi\cdot n)}{2\cdot\pi^2\cdot n^2}$

Expectation of x²:

$$\int_0^L x^2\cdot(\psi(n,x,L))^2 dx \rightarrow \frac{3\cdot L^2\cdot\sin(2\cdot\pi\cdot n) + 4\cdot\pi^3\cdot L^2\cdot n^3 - 6\cdot\pi^2\cdot L^2\cdot n^2\cdot\sin(2\cdot\pi\cdot n) - 6\cdot\pi\cdot L^2\cdot n\cdot\cos(2\cdot\pi\cdot n)}{12\cdot\pi^3\cdot n^3}$$

Expectation of first derivative: $\int_0^L \psi(n,x,L)\cdot\left(\frac{d}{dx}\psi(n,x,L)\right) dx \rightarrow \frac{\sin(\pi\cdot n)^2}{L}$

Expectation of second derivative: $\int_0^L \psi(n,x,L)\cdot\frac{d^2}{dx^2}\psi(n,x,L) dx \rightarrow \frac{\pi\cdot n\cdot(\sin(2\cdot\pi\cdot n) - 2\cdot\pi\cdot n)}{2\cdot L^2}$

The above section of the worksheet reveals that, because sin(integer × π) = 0, expectation values of the *n*th state include

$$\langle x\rangle_n = L/2,\quad \langle x^2\rangle_n = \{\tfrac{1}{3} - \tfrac{1}{2}(n\pi)^{-2}\}L^2,\quad \langle \mathrm{d}/\mathrm{d}x\rangle_n = 0,\quad \text{and}\quad \langle \mathrm{d}^2/\mathrm{d}x^2\rangle_n = -(n\pi/L)^2$$

and, since $\hat{p}_x = (\hbar/\mathrm{i}) \times (\mathrm{d}/\mathrm{d}x)$ [7.29],

$$\langle p_x\rangle_n = 0,\quad \langle p_x^2\rangle_n = (n\pi\hbar/L)^2$$

Neither the mean position, nor the mean momentum, of the *n*th state depend on *n*. Before we examine superpositions of these states, we need to check that the Heisenberg uncertainty principle,

$$\Delta p_x \Delta x = \{\langle p_x^2\rangle - \langle p_x\rangle^2\}^{1/2}\{\langle x^2\rangle - \langle x\rangle^2\}^{1/2} \geq \tfrac{1}{2}\hbar \text{ [7.39]},$$

is satisfied and we must also take a careful look at the dependency of ψ_n on x.

$$(\Delta p_x \Delta x)_n = \left\{\frac{(n\pi\hbar)^2}{L^2} - 0\right\}^{1/2}\left\{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4}\right\}^{1/2} = \left\{\frac{1}{12} - \frac{1}{2n^2\pi^2}\right\}^{1/2} n\pi\hbar$$

The product $(\Delta p_x \Delta x)_n/\hbar$ equals 0.57, 1.67, 2.63, and 3.56, respectively, for the states *n* equals 1, 2, 3, and 4, which demonstrates that the Heisenberg uncertainty principle is satisfied.

Mathcad plots of the wavefunctions for n equals 1, 2, and 3 are presented in Figure 7.1. They show a progressive increase in their curvature so we immediately conclude that the higher the value of n, the greater the energy of the state. Furthermore, they show a particular type of symmetry around the point $x = L/2$, the centre of symmetry in this exercise. If you compare the value of $\psi_n\left(\frac{L}{2}+\delta\right)$ with the value of $\psi_n\left(\frac{L}{2}-\delta\right)$, where δ is any length, you will find that $\psi_n\left(\frac{L}{2}+\delta\right) = \psi_n\left(\frac{L}{2}-\delta\right)$ for odd values of n and $\psi_n\left(\frac{L}{2}+\delta\right) = -\psi_n\left(\frac{L}{2}-\delta\right)$ for even values of n. When the sign of the equality is positive under this so-called inversion operation through the centre of symmetry, the wavefunction is said to have either even parity or gerade symmetry. When the sign of the equality is negative under the inversion operation, the wavefunction is said to have either odd parity or ungerade symmetry. Odd-numbered eigenstates have gerade symmetry while even-numbered eigenstates have ungerade symmetry.

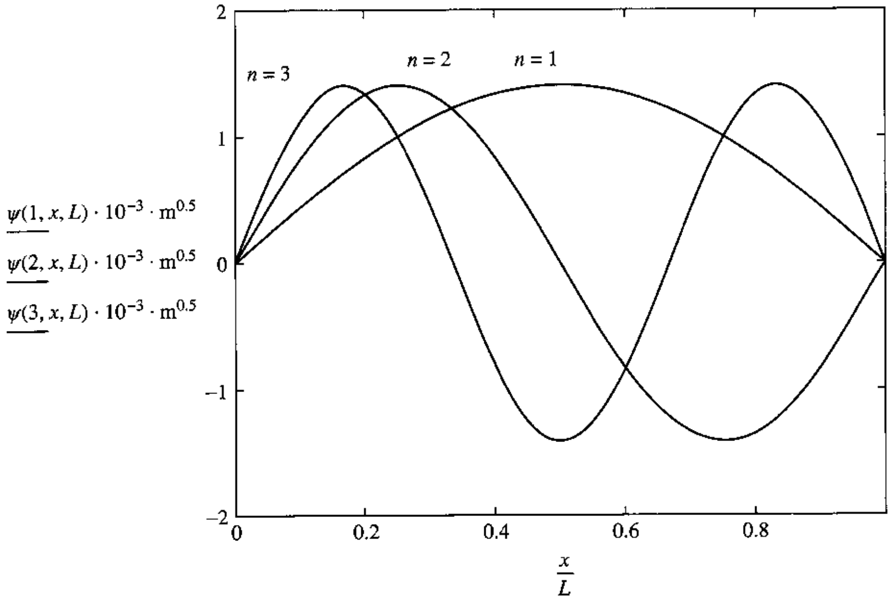


Figure 7.1

This eigenstate property of gerade or ungerade symmetry has arisen because of the conditions imposed by the boundary conditions, conditions that must also be satisfied by a wavefunction Ψ_r that is a superposition of r eigenstates, each of which has the form ψ_n. However, to satisfy the parity requirement Ψ_r must be a superposition of either gerade eigenstates alone (those with odd values of n) or ungerade eigenstates alone (those with even values of n). This will provide Ψ_r with a unique gerade or ungerade symmetry. The following is a section of the Mathcad worksheet for the study of gerade superpositions in which the electron has an equal probability of being found in any one of the eigenstates of the superposition because the coefficient of the eigenstates are equal. The factor $(1/r)^{1/2}$ is the normalization constant for the superposition of r eigenstates and the probability that the electron will be found in a particular eigenstate is $1/r$.

$$\Psi(r,x,L) := \left(\frac{1}{r}\right)^{1/2} \cdot \sum_{n=1}^{r} \psi(2\cdot n-1,x,L) \qquad \textbf{Normality check:} \quad \int_0^L \Psi(5,x,L)^2 dx = 1$$

Nanotube length: $L := 1\cdot 10^{-6}\cdot m$ **Axis range:** $x := 0,0.001\cdot L\cdot L$

Mathcad plots of the probability density Ψ_r^2 are shown in Figure 7.2 for the superposition of 2, 4, and 8 eigenstates. Examination of the probability density plots reveals that, when the superposition has few terms, the particle position is ill-defined. There is a great uncertainty in knowledge of position. When many terms are added to the superposition, the uncertainty narrows to a narrow space at each end of the nanotube ($x = 0$ and $x = L$). When the electron state is the superposition of a great many eigenstates, there is a probabilty of $\frac{1}{2}$ that a measurement will find the electron at an end of the nanotube!

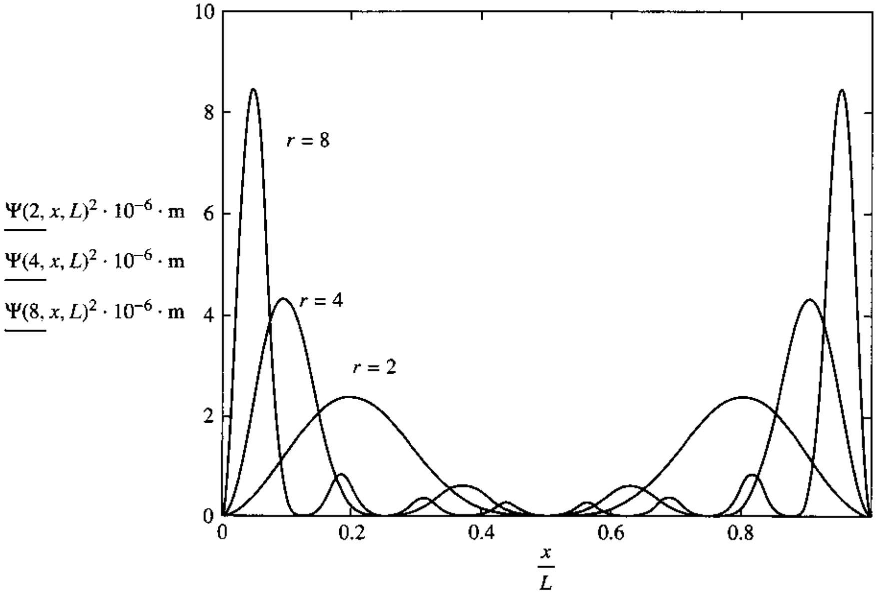


Figure 7.2

The plot of probability density against position clearly indicates that the superposition is symmetrical around the centre of symmetry, i.e. at the point $x = L/2$. Consequently, the expectation position for all superpositions is $x = L/2$. The expectation value for position is independent of the number of terms in the superposition.

The square root of the expectation value of x^2 is called the root-mean-square value of x, x_{rms}. It depends on the number of terms in the superposition, r, so we write it as a function of r, $x_{\text{rms}}(r)$:

$$x_{\text{rms}}^2(r) = \langle x^2 \rangle = \int_0^L x^2\,|\psi_r|^2 dx = \frac{1}{r}\sum_{p=1}^{r}\sum_{q=1}^{r}\int_0^L x^2 \psi_{2p-1}\psi_{2q-1} dx = \frac{1}{r}\sum_{p=1}^{r}\sum_{q=1}^{r} I_{pq}$$

where $$I_{pq} = \int_0^L x^2 \psi_{2p-1}\psi_{2q-1} dx = \frac{2}{L}\int_0^L x^2 \sin\{(2p-1)\pi x/L\}\sin\{(2q-1)\pi x/L\} dx$$

The above double summation over $p = 1, 2, \dots, r$ and $q = 1, 2, \dots, r$ can be placed into summations that reduce the possibility of term omission. This is accomplished by imagining the double sum $\sum_{p=1}^{r}\sum_{q=1}^{r} I_{pq}$ to be arranged into rows such that the first row consists terms for which $p = 1$ and successive terms in the row have $q = 1, 2, \dots, r$. The second row consists of terms for which $p = 2$ and successive terms in the row have $q = 1, 2, \dots, r$. The last row consists of terms for which $p = \mathrm{r}$ and successive terms in the row have $q = 1, 2, \dots, r$. This 'matrix' of elements consists of a diagonal and two off-diagonal triangular areas ... an upper triangular area that is above the diagonal and a lower triangular area that lies below the diagonal. The above definition of I_{pq} shows that there is no change when q is interchanged with p. Consequently, $I_{pq} = I_{qp}$ and the sum of terms in the lower triangle equals the sum of terms in the upper triangular. These observations prompt a rearrangement of the double sum into a sum of diagonal elements plus twice the sum of terms in the upper triangle.

$$x_{\mathrm{rms}}^2(r) = \frac{1}{r}\left\{\sum_{p=1}^{r} I_{pp} + 2\sum_{p=1}^{r-1}\sum_{q=p+1}^{r} I_{pq}\right\}$$

$$= \frac{L^2}{r}\left\{\sum_{p=1}^{r}\left\{\frac{2\pi^2(2p-1)^2 - 3}{6\pi^2(2p-1)^2}\right\} + 2\sum_{p=1}^{r-1}\sum_{q=p+1}^{r}\left\{\frac{8(2p-1)(2q-1)}{\pi^2\{(2p-1)^2 - (2q-1)^2\}^2}\right\}\right\}$$

The Figure 7.3 Mathcad plot of χ_{rms} against r (where χ_{rms} is defined to equal x_{rms}/L) indicates that this expectation value depends on the number of terms in the superposition. Moreover, as r approaches infinity, x_{rms} approaches $\sqrt{2}L/2$.

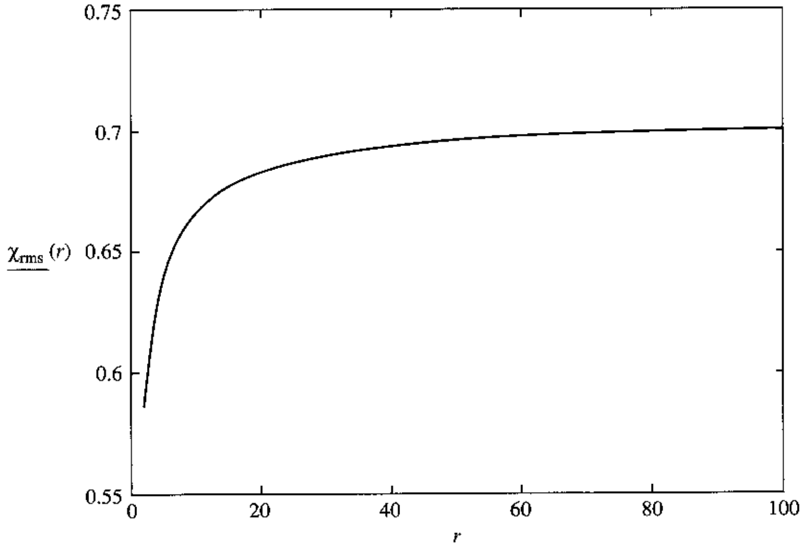


Figure 7.3

In the limit of an infinite number of superpositioned eigenfunctions the uncertainty in the electron position is

$$\Delta x = \{\langle x^2\rangle - \langle x\rangle^2\}^{1/2} = \left\{\left(\frac{\sqrt{2}L}{2}\right)^2 - \left(\frac{L}{2}\right)^2\right\}^{1/2} = \frac{L}{2}$$

8

Quantum theory: techniques and applications

Answers to discussion questions

D8.2 The correspondence principle (Section 8.1) states that in the limit of very large quantum numbers quantum mechanics merges with classical mechanics. The harmonic oscillator provides an example. A classical harmonic oscillator's range of motion is restricted by classical turning points, which are determined by the oscillator's total energy; that energy can take on any real positive value. By contrast, a quantum harmonic oscillator can tunnel past classical turning points into the classically forbidden region with a non-zero probability. The total energy of a quantum harmonic oscillator is quantized; not every real positive value is allowed. At high quantum numbers, the probability of tunnelling beyond the classical turning points falls (approaching the zero probability of classical harmonic oscillators). Furthermore, the most likely place to find the oscillator is near the classical turning points. (This is true of the classical oscillator as well: because the speed of the oscillator vanishes at the turning points, the oscillator spends more time near the turning points than elsewhere in its range.) See Figure 8.23, particularly for $v = 20$, to see the probability distribution for large v approach the classical picture. Finally, although the spacing between discrete allowed energy levels is the same size at large quantum numbers as at small ones, that spacing is a smaller fraction of total energy at large quantum numbers; in that sense, the allowed energy levels are more nearly continuous at large quantum numbers than small.

D8.4 The physical origin of tunnelling is related to the probability density of the particle, which according to the Born interpretation is the square of the wavefunction that represents the particle. This interpretation requires that the wavefunction of the system be everywhere continuous, even at barriers. Therefore, if the wavefunction is non-zero on one side of a barrier it must be non-zero on the other side of the barrier and this implies that the particle has tunnelled through the barrier. The transmission probability depends on the mass of the particle (specifically $m^{1/2}$, through eqns 8.15 and 8.19): the greater the mass the smaller the probability of tunnelling. Electrons and protons have small masses, molecular groups large masses; therefore, tunnelling effects are more observable in process involving electrons and protons.

D8.6 Macroscopic synthesis and material development always contains elements of molecular randomness. Crystal structures are never perfect. A product of organic synthesis is never absolutely free of impurities, although impurities may be at a level that is lower than measurement techniques make possible. Alloys are grainy and slightly non-homogeneous within any particular grain. Furthermore, the random distribution of atomic/molecular positions and orientations within, and between, macroscopic objects causes the conversion of energy to non-useful heat during manufacturing processes. Production efficiencies are difficult to improve. Nanometre technology on the 1 nm to 100 nm scale may resolve many of these problems. Self-organization and production processes by nanoparticles and nanomachines may be able to exclude impurities and greatly improve homogeneity by effective examination and selection of each atom/molecule during nanosynthesis and nanoproduction processes. Higher efficiencies of energy usage may be achievable as nanomachines produce idealized materials at the smaller sizes and pass their products to larger nanomachines for production of larger-scale materials.

The directed, non-random, use of atoms and molecules by nanotechniques holds the promise for the production of smaller transistors and wires for the electronics and computer industries. Unusual material strengths, optical properties, magnetic properties, and catalytic properties may be achievable. Higher efficiencies of photo-electronic conversion would be a boon to mankind. There is hope that science will devise nanoparticles that destroy pathogens and repair tissues. See *Impact* 8.1 for discussion of nano-quantum dots that have unusual optical and magnetic properties. See *Impact* 8.2 for discussion of scanning probe microscopy, a technology for the examination of atom positions on a macroscopic surface and for positioning atoms on a surface.

Solutions to exercises

E8.1(b)

$$E = \frac{n^2h^2}{8m_eL^2}\ [8.4a]$$

$$\frac{h^2}{8m_eL^2} = \frac{(6.626\times10^{-34}\ \text{J s})^2}{8(9.109\times10^{-31}\ \text{kg})\times(1.50\times10^{-9}\ \text{m})^2} = 2.68\times10^{-20}\ \text{J}$$

The conversion factors required are

$$1\ \text{eV} = 1.602\times10^{-19}\ \text{J};\quad 1\ \text{cm}^{-1} = 1.986\times10^{-23}\ \text{J};\quad 1\ \text{eV} = 96.485\ \text{kJ mol}^{-1}$$

(a) $$E_3 - E_1 = (9-1)\frac{h^2}{8m_eL^2} = 8(2.68\times10^{-20}\ \text{J})$$

$$= \boxed{2.14\times10^{-19}\ \text{J}} = \boxed{1.34\ \text{eV}} = \boxed{1.08\times10^{4}\ \text{cm}^{-1}} = \boxed{129\ \text{kJ mol}^{-1}}$$

(b) $$E_7 - E_6 = (49-36)\frac{h^2}{8m_eL^2} = 13(2.68\times10^{-20}\ \text{J})$$

$$= \boxed{3.48\times10^{-19}\ \text{J}} = \boxed{2.17\ \text{eV}} = \boxed{1.75\times10^{4}\ \text{cm}^{-1}} = \boxed{210\ \text{kJ mol}^{-1}}$$

E8.2(b) The wavefunctions are

$$\psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\ [8.4b]$$

The required probability is

$$P = \int \psi^*\psi\,\text{d}x = \frac{2}{L}\int \sin^2\left(\frac{n\pi x}{L}\right)\text{d}x \approx \frac{2\Delta x}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

where $\Delta x = 0.02\,L$ and the function is evaluated at $x = 0.66\,L$.

(a) For $n = 1$ $P = \dfrac{2(0.02L)}{L}\sin^2(0.66\pi) = \boxed{0.03\overline{1}}$

(b) For $n = 2$ $P = \dfrac{2(0.02L)}{L}\sin^2[2(0.66\pi)] = \boxed{0.02\overline{9}}$

E8.3(b) The expectation value is

$$\langle p\rangle = \int \psi^* \hat{p}\psi\,\mathrm{d}x$$

but first we need $\hat{p}\psi$

$$\hat{p}\psi = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right) = -\mathrm{i}\hbar\left(\frac{2}{L}\right)^{1/2}\frac{n\pi}{L}\cos\left(\frac{n\pi x}{L}\right)$$

so $\langle p\rangle = \dfrac{-2\mathrm{i}\hbar n\pi}{L^2}\displaystyle\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \boxed{0}$ for all n.

and $\langle p^2\rangle = 2m\langle H\rangle = 2mE_n = \dfrac{h^2n^2}{4L^2}$ for all n.

So, for $n = 2$

$$\langle p^2\rangle = \boxed{\frac{h^2}{L^2}}$$

E8.4(b) The wavefunction is

$$\psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right) \text{ [8.4b]}$$

Hence, $\langle x\rangle = \displaystyle\int \psi^* x\psi\,\mathrm{d}x = \frac{2}{L}\int_0^L x\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$

An integral table gives

$$\int x\sin^2 ax\,\mathrm{d}x = \frac{x^2}{4} - \frac{x\sin 2ax}{4a} - \frac{\cos 2ax}{8a^2}$$

so $\langle x\rangle = \dfrac{2}{L}\left[\dfrac{x^2}{4} - \dfrac{Lx}{4n\pi}\sin\left(\dfrac{2n\pi x}{L}\right) - \dfrac{L^2}{8(n\pi)^2}\cos\left(\dfrac{2n\pi x}{L}\right)\right]\Bigg|_0^L = \boxed{\dfrac{L}{2}}$ for all n.

$$\langle x^2\rangle = \frac{2}{L}\int_0^L x^2\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

An integral table gives

$$\int x^2\sin^2 ax\,\mathrm{d}x = \frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin 2ax - \frac{x\cos 2ax}{4a^2}$$

so $$\langle x^2\rangle = \frac{2}{L}\left[\frac{x^3}{6} - \left(\frac{Lx^2}{4n\pi} - \frac{L^3}{(2n\pi)^3}\right)\sin\left(\frac{2n\pi x}{L}\right) - \frac{L^2x}{(2n\pi)^2}\cos\left(\frac{2n\pi x}{L}\right)\right]\Bigg|_0^L$$

$$= \frac{2}{L}\left(\frac{L^3}{6} - \frac{L^3}{(2n\pi)^2}\right) = L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

For $n = 2$, $\langle x^2\rangle = \boxed{L^2\left(\frac{1}{3} - \frac{1}{8\pi^2}\right)}$

E8.5(b) The zero-point energy is the ground-state energy, that is, with $n_x = n_y = n_z = 1$:

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2}\,[8.11\text{b with equal lengths}] = \frac{3h^2}{8mL^2}$$

Set this equal to the rest energy mc^2 and solve for L:

$$mc^2 = \frac{3h^2}{8mL^2} \quad \text{so} \quad L = \boxed{\left(\frac{3}{8}\right)^{1/2}\frac{h}{mc} = \left(\frac{3}{8}\right)^{1/2}\lambda_C}$$

where λ_C is the Compton wavelength of a particle of mass m.

E8.6(b) $$\psi_5 = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{5\pi x}{L}\right)\,[8.4\text{b}]$$

$$P(x) \propto \psi_5^2 \propto \sin^2\left(\frac{5\pi x}{L}\right)$$

Maxima and minima in $P(x)$ correspond to $\frac{\mathrm{d}P(x)}{\mathrm{d}x} = 0$

$$\frac{\mathrm{d}}{\mathrm{d}x}P(x) \propto \frac{\mathrm{d}\psi^2}{\mathrm{d}x} \propto \sin\left(\frac{5\pi x}{L}\right)\cos\left(\frac{5\pi x}{L}\right) \propto \sin\left(\frac{10\pi x}{L}\right) \quad [2\sin\alpha\cos\alpha = \sin 2\alpha]$$

Now, $\sin\theta = 0$ when $\theta = 0, \pi, 2\pi$, etc. (i.e. when $\theta = n'\pi$, where n' is an integer).

Thus, $\frac{10\pi x}{L} = n'\pi$ for $n' \le 10$ so $x = \frac{n'L}{10}$

$x = 0$ and $x = L$ are minima. Maxima and minima alternate, so maxima correspond to

$n' = 1, 3, 5, 7, 9$, so $x = \boxed{\frac{L}{10}, \frac{3L}{10}, \frac{L}{2}, \frac{7L}{10}, \frac{9L}{10}}$

COMMENT. Maxima in ψ^2 correspond to maxima *and* minima in ψ itself, so one can also solve this exercise by finding all points where $\dfrac{\mathrm{d}\psi}{\mathrm{d}x} = 0$.

8.7(b) In the original cubic box

$$E_1 = (n_1^2 + n_2^2 + n_3^2) \times \left(\frac{h^2}{8mL^2}\right) = \frac{K}{L^2}, \quad K = (n_1^2 + n_2^2 + n_3^2) \times \left(\frac{h^2}{8m}\right)$$

In the smaller cubic box

$$E_2 = \frac{K}{(0.9L)^2}.$$

Hence, $\Delta E = \dfrac{K}{L^2}\left(\dfrac{1}{0.9^2} - 1\right)$,

and the relative change is

$$\frac{\Delta E}{E} = \frac{1}{(0.9)^2} - 1 = 0.235 = \boxed{23.5\%}$$

8.8(b) $E = \frac{3}{2}kT$ is the average translational energy of a gaseous molecule (see Chapter 17).

$$E = \tfrac{3}{2}kT = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2h^2}{8mL^2}$$

so $n = \dfrac{(12kTm)^{1/2}L}{h}$.

Before we evaluate this expression, we need the mass of a nitrogen molecule:

$$m = \frac{2 \times 14.01 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}}{6.022 \times 10^{23}\,\mathrm{mol^{-1}}} = 4.653 \times 10^{-26}\,\mathrm{kg}$$

Now, $n = \dfrac{(12 \times 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 300\,\mathrm{K} \times 4.653 \times 10^{-26}\,\mathrm{kg})^{1/2} \times 1.00\,\mathrm{m}}{6.626 \times 10^{-34}\,\mathrm{J\,s}} = \boxed{7.26 \times 10^{10}}$

The difference between neighbouring levels is

$$\Delta E_n = E_{n+1} - E_1 = \frac{\{(n+1)^2 - n^2\}h^2}{8mL^2} = \frac{(2n+1)h^2}{8mL^2}.$$

So here,

$$\Delta E = \frac{(2 \times 7.26 \times 10^{10} + 1) \times (6.626 \times 10^{-34}\,\mathrm{J\,s})^2}{8 \times 4.653 \times 10^{-26}\,\mathrm{kg} \times (1.00\,\mathrm{m})^2} = \boxed{1.71 \times 10^{-31}\,\mathrm{J}}$$

The de Broglie wavelength is obtained from

$$\lambda = \frac{h}{p} = \frac{h}{mv}\ [7.16]$$

The velocity is obtained from

$$E_K = \tfrac{1}{2}mv^2 = \tfrac{3}{2}kT = \tfrac{3}{2}(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(300\ \mathrm{K}) = 6.21\times10^{-21}\ \mathrm{J}$$

$$\text{So,}\quad v = \left(\frac{2E_K}{m}\right)^{1/2} = \left(\frac{2\times6.21\times10^{-21}\ \mathrm{J}}{4.653\times10^{-26}\ \mathrm{kg}}\right)^{1/2} = 517\ \mathrm{m\ s^{-1}}$$

$$\text{and}\quad \lambda = \frac{6.626\times10^{-34}\ \mathrm{J\ s}}{(4.653\times10^{-26}\ \mathrm{kg})\times(517\ \mathrm{m\ s^{-1}})} = 2.76\times10^{-11}\ \mathrm{m} = \boxed{27.6\ \mathrm{pm}}$$

COMMENT. The conclusion to be drawn from all of these calculations is that the translational motion of the nitrogen molecule can be described classically. The energy of the molecule is essentially continuous,

$$\frac{\Delta E}{E} \lll 1$$

E8.9(b)

$$E = \left(v+\frac{1}{2}\right)\hbar\omega,\quad \omega = \left(\frac{k_f}{m}\right)^{1/2}\ [8.24]$$

The zero-point energy corresponds to $v = 0$, hence

$$E_0 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k_f}{m}\right)^{1/2} = \tfrac{1}{2}(1.0546\times10^{-34}\ \mathrm{J\ s})\times\left(\frac{285\ \mathrm{N\ m^{-1}}}{5.16\times10^{-26}\ \mathrm{kg}}\right)^{1/2} = \boxed{3.92\times10^{-21}\ \mathrm{J}}$$

E8.10(b) The difference in adjacent energy levels is

$$\Delta E = E_{v+1} - E_v = \hbar\omega\ [8.25] = \hbar\left(\frac{k_f}{m}\right)^{1/2}\ [8.24]$$

$$\text{so}\quad k_f = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88\times10^{-25}\ \mathrm{kg})\times(3.17\times10^{-21}\ \mathrm{J})^2}{(1.0546\times10^{-34}\ \mathrm{J\ s})^2} = 260\ \mathrm{kg\ s^{-2}} = \boxed{260\ \mathrm{N\ m^{-1}}}$$

E8.11(b) The requirement for a transition to occur is that $\Delta E(\text{system}) = E(\text{photon})$,

$$\text{so}\quad \Delta E(\text{system}) = \hbar\omega\ [8.25] = E(\text{photon}) = h\nu = \frac{hc}{\lambda}$$

$$\text{Therefore,}\ \frac{hc}{\lambda} = \frac{h\omega}{2\pi} = \left(\frac{h}{2\pi}\right)\times\left(\frac{k_f}{m}\right)^{1/2}\ [8.24]$$

$$\lambda = 2\pi c\left(\frac{m}{k_f}\right)^{1/2} = (2\pi)\times(2.998\times10^{8}\ \mathrm{m\ s^{-1}})\times\left(\frac{15.9949\times1.6605\times10^{-27}\ \mathrm{kg}}{544\ \mathrm{N\ m^{-1}}}\right)^{1/2}$$

$$= 1.32\times10^{-5}\ \mathrm{m} = \boxed{13.2\ \mu\mathrm{m}}$$

E8.12(b) The frequency of a harmonic oscillator is

$$\omega = \left(\frac{k_f}{m}\right)^{1/2}$$

^{1}H (H) and ^{3}H (T) are isotopes, so we expect that the force constant is the same in H_2 and T_2. They differ in mass, so the frequencies are inversely proportional to the square root of the mass:

$$\omega_T = \omega_H\left(\frac{m_H}{m_T}\right)^{1/2}$$

But the mass is not the mass of the molecule. We need a result from Chapter 12 to incorporate the mass (eqn 12.32). The appropriate mass for the oscillation of a diatomic molecule is

$$m_{\text{eff}} = \frac{m_1m_2}{m_1+m_2} = \frac{m}{2}\,[m_1 = m_2 = m]$$

For H_2: $m_{\text{eff}} = \dfrac{m}{2} = \dfrac{1.0078\times(1.6605\times10^{-27}\,\text{kg})}{2} = \boxed{8.3673\times10^{-28}\,\text{kg}}$

For T_2: $m_{\text{eff}} = \dfrac{m}{2} = \dfrac{3.0160\times(1.6605\times10^{-27}\,\text{kg})}{2} = \boxed{2.5040\times10^{-27}\,\text{kg}}$

$$\omega_T = 131.9\,\text{THz}\times\left(\frac{8.3673\times10^{-28}\,\text{kg}}{2.5040\times10^{-27}\,\text{kg}}\right)^{1/2} = \boxed{76.2\,\text{THz}}$$

E8.13(b) $\Delta E = \hbar\omega = h\nu$

(a) $\Delta E = h\nu = (6.626\times10^{-34}\,\text{J Hz}^{-1})\times(33\times10^3\,\text{Hz}) = \boxed{2.2\times10^{-29}\,\text{J}}$

(b) For a two-particle oscillator m_{eff}, replaces m in the expression for ω. (See Chapter 12 for a more complete discussion of the vibration of a diatomic molecule.)

$$\Delta E = \hbar\omega = \hbar\left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2}[8.24] = \hbar\left(\frac{2k}{m}\right)^{1/2}$$

The last equality uses eqn 12.32 for two equal masses, as in Exercise 8.12(b).

$$\Delta E = (1.055\times10^{-34}\,\text{J s})\times\left(\frac{(2)\times(1177\,\text{N m}^{-1})}{(16.00)\times(1.6605\times10^{-27}\,\text{kg})}\right)^{1/2} = \boxed{3.14\times10^{-20}\,\text{J}}$$

E8.14(b) The first excited-state wavefunction has the form

$$\psi_1 = 2N_1 y\exp(-\tfrac{1}{2}y^2)\ [8.30]$$

where N_1 is a collection of constants and $y \equiv x\left(\dfrac{m\omega}{\hbar}\right)^{1/2}$. To see if it satisfies the Schrödinger equation, we apply the energy operator to this function

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \tfrac{1}{2}m\omega^2x^2\psi$$

We need derivatives of ψ

$$\frac{d\psi}{dx} = \frac{d\psi}{dy}\frac{dy}{dx} = \left(\frac{m\omega}{\hbar}\right)^{1/2}(2N_1)\times(1-y^2)\times\exp(-\tfrac{1}{2}y^2)$$

and $$\frac{d^2\psi}{dx^2}=\frac{d^2\psi}{dy^2}\left(\frac{dy}{dx}\right)^2=\left(\frac{m\omega}{\hbar}\right)\times(2N_1)\times(-3y+y^3)\times\exp(-\tfrac{1}{2}y^2)=\left(\frac{m\omega}{\hbar}\right)\times(y^2-3)\psi$$

So, $$\begin{aligned}\hat{H}\psi&=-\frac{\hbar^2}{2m}\times\left(\frac{m\omega}{\hbar}\right)\times(y^2-3)\psi+\tfrac{1}{2}m\omega^2x^2\psi\\&=-\tfrac{1}{2}\hbar\omega\times(y^2-3)\times\psi+\tfrac{1}{2}\hbar\omega y^2\psi=\tfrac{3}{2}\hbar\omega\psi\end{aligned}$$

Thus, ψ is a solution the Schrödinger equation with energy eigenvalue $E=\tfrac{3}{2}\hbar\omega$.

E8.15(b) The harmonic oscillator wavefunctions have the form

$$\psi_v(x)=N_vH_v(y)\exp(-\tfrac{1}{2}y^2)\quad\text{with}\quad y=\frac{x}{\alpha}\quad\text{and}\quad\alpha=\left(\frac{\hbar^2}{mk_f}\right)^{1/4}\quad[8.27]$$

The exponential function approaches zero only as x approaches $\pm\infty$, so the nodes of the wavefunction are the nodes of the Hermite polynomials.

$$H_5(y)=32y^5-160y^3+120y=0\ [\text{Table 8.1}]=8y(4y^4-20y^2+15)$$

So, one solution is $y=0$, which leads to $x=0$. The other factor can be made into a quadratic equation by letting $z=y^2$

$$4z^2-20z+15=0$$

so $$z=\frac{-b\pm\sqrt{b^2-4ac}}{2a}=\frac{20\pm\sqrt{20^2-4\times4\times15}}{2\times4}=\frac{5\pm\sqrt{10}}{2}$$

Evaluating the result numerically yields $z=0.92$ or 4.08, so $y=\pm0.96$ or ±2.02. Therefore $x=\boxed{0,\pm0.96\alpha,\text{ or }\pm2.02\alpha}$.

COMMENT. Numerical values could also be obtained graphically by plotting $H_5(y)$.

E8.16(b) The most probable displacements are the values of x that maximize ψ^2. As noted in Exercise 8.6(b), maxima in ψ^2 correspond to maxima *and* minima in ψ itself, so one can solve this exercise by finding all points where $\frac{d\psi}{dx}=0$. From eqn 8.27 and Table 8.1, the wavefunction is

$$\psi_3(x)=N_3H_3(y)\exp(-\tfrac{1}{2}y^2)\quad\text{with}\quad y=\frac{x}{\alpha},\ \alpha=\left(\frac{\hbar^2}{mk_f}\right)^{1/4},\ \text{and } H_3(y)=8y^3-12y$$

$$\frac{d\psi_3}{dx}=\frac{dy}{dx}\frac{d\psi_3}{dy}=\frac{N_3}{\alpha}\{(24y^2-12)\exp(-\tfrac{1}{2}y^2)-(8y^3-12y)y\exp(-\tfrac{1}{2}y^2)\}=0$$

Dividing through by constants and the exponential functions yields

$$-8y^4+36y^2-12=0$$

Letting $z=y^2$ (and dividing through by -4) yields the quadratic equation

$$2z^2-9z+3=0$$

so $$z=\frac{-b\pm\sqrt{b^2-4ac}}{2a}=\frac{9\pm\sqrt{9^2-2\times3\times4}}{2\times2}=\frac{9\pm\sqrt{57}}{4}$$

Evaluating the result numerically yields $z = 4.14$ or 0.363, so $y = \pm 2.03$ or ± 0.602, therefore $x = \boxed{0, \pm 2.03\alpha, \text{ or } \pm 0.602\alpha}$.

8.17(b) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega\,[8.26] = \frac{\hbar}{2}\left(\frac{k}{m_{\text{eff}}}\right)^{1/2}\;[8.24]$$

$$m_{\text{eff}} = 14.0031 \times (1.6605 \times 10^{-27}\text{ kg})/2 = 1.1626 \times 10^{-26}\text{ kg}$$

$$E_0 = \frac{1.0546 \times 10^{-34}\text{ J s}}{2} \times \left(\frac{2293.8\text{ N m}^{-1}}{1.1626 \times 10^{-26}\text{ kg}}\right)^{1/2} = \boxed{2.3422 \times 10^{-20}\text{ J}}$$

8.18(b) Orthogonality requires that

$$\int \psi_m^* \psi_n \,\mathrm{d}\tau = 0\;[7.34]$$

if $m \neq n$.

Performing the integration

$$\int \psi_m^* \psi_n \,\mathrm{d}\tau = \int_0^{2\pi} N\mathrm{e}^{-\mathrm{i}m\phi} N\mathrm{e}^{\mathrm{i}n\phi}\,\mathrm{d}\phi = N^2 \int_0^{2\pi} \mathrm{e}^{\mathrm{i}(n-m)\phi}\,\mathrm{d}\phi$$

If $m \neq n$, then

$$\int \psi_m^* \psi_n \,\mathrm{d}\tau = \frac{N^2}{\mathrm{i}(n-m)}\mathrm{e}^{\mathrm{i}(n-m)\phi}\bigg|_0^{2\pi} = \frac{N^2}{\mathrm{i}(n-m)}(1-1) = 0$$

Therefore, they are orthogonal.

8.19(b) The energy levels of a particle on a ring are given by eqn 8.38a:

$$E = \frac{m_l^2\hbar^2}{2I} = \frac{m_l^2\hbar^2}{2mr^2}, \quad m_l = 0, \pm 1, \pm 2, \ldots$$

We set this quantity equal to the classical energy and solve for $|m_l|$:

$$E = \frac{m_l^2\hbar^2}{2mr^2} = \frac{kT}{2} \quad \text{so}$$

$$|m_l| = \frac{r(kTm)^{1/2}}{\hbar}$$

$$= \frac{(100 \times 10^{-12}\text{ m}) \times \{(1.381 \times 10^{-23}\text{ J K}^{-1}) \times (298\text{ K}) \times (1.6726 \times 10^{-27}\text{ kg})\}^{1/2}}{1.0546 \times 10^{-34}\text{ J s}}$$

$$= \boxed{2.49}$$

Of course, m_l must be an integer, so $m_l = \pm 2$ is the closest energy level.

COMMENT. The correspondence principle (Section 8.1) states that quantum systems behave classically in the limit of large quantum numbers. One manifestation of classical behaviour is the smallness of excitation energies compared to typical system energies, which makes system energies appear to take on a continuum of values rather than a set of discrete values. The system in this exercise is not nearly as classical as the one described in Exercise 8.8(b), but it is much more classical than that of part (b) in Exercise 8.13(b).

E8.20(b) In Chapter 12, we will see that the results on rotational motion developed in this chapter apply to rigid rotors of various shapes, not just to point masses. So, we can use the quantum expression for angular momentum, $J_z = m_l\hbar$, and set it equal to the classical expression, $J_z = I\omega = mr^2\omega/2$. Solving for m_l yields

$$m_l = \frac{mr^2\omega}{2\hbar} = \frac{mr^2\pi\nu}{\hbar} = \frac{(0.130\ \text{kg}) \times (15 \times 10^{-2}\ \text{m})^2 \times \pi \times 33\ \text{min}^{-1}}{1.0546 \times 10^{-34}\ \text{J s}} \times \frac{1\ \text{min}}{60\ \text{s}}$$
$$= \boxed{4.8 \times 10^{31}}$$

E8.21(b) In Chapter 12, we will see that the results on rotational motion developed in this chapter apply to rigid rotors of various shapes, not just to point masses. The rotor in this case is not a disk-like object (as in Exercise 8.20(b)), so we use results derived for rotation in three dimensions. The energy levels are

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \dots\ [8.53]$$

The minimum energy to start it rotating is the minimum excitation energy, the energy to take it from the motionless $l = 0$ to the rotating $l = 1$ state:

$$\Delta E = E_1 = \frac{1 \times 2 \times (1.0546 \times 10^{-34}\ \text{J s})^2}{2 \times (3.07 \times 10^{-45}\ \text{kg m}^2)} = \boxed{3.62 \times 10^{-24}\ \text{J}}$$

E8.22(b) The energy levels are

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \dots\ [8.53]$$

So, the excitation energy is

$$\Delta E = E_2 - E_1 = \frac{(3 \times 4 - 2 \times 3) \times (1.0546 \times 10^{-34}\ \text{J s})^2}{2 \times (3.07 \times 10^{-45}\ \text{kg m}^2)} = \boxed{1.09 \times 10^{-23}\ \text{J}}$$

E8.23(b) The energy levels are

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \dots\ [8.53]$$

So, the minimum energy *allowed* for this system is zero—but that corresponds to rest, not rotation. So, the minimum energy of rotation occurs for the state that has $l = 1$. The angular momentum in that state is

$$J = \{l(l+1)\}^{1/2}\hbar\ [8.54\text{a}] = \boxed{2^{1/2}\hbar} = 2^{\frac{1}{2}} \times (1.0546 \times 10^{-34}\ \text{J s}) = \boxed{1.49 \times 10^{-34}\ \text{J s}}.$$

COMMENT. Note that the moment of inertia does not enter into the result. Thus, the minimum angular momentum is the same for a molecule of CH_4 as for a molecule of C_{60} as for a football.

8.24(b) The cones are constructed as described in Section 8.7(d) and Figure 8.37(b) of the text; their edges are of length $\{6(6+1)\}^{1/2} = 6.48$ and their projections are $m_j = +6, +5, \ldots, -6$. See Figure 8.1(a).

The vectors follow, in units of $\hbar$. From the highest-pointing to the lowest-pointing vectors (Figure 8.1(b)), the values of m_l are 6, 5, 4, 3, 2, 1, 0, −1, −2, −3, −4, −5, and −6.

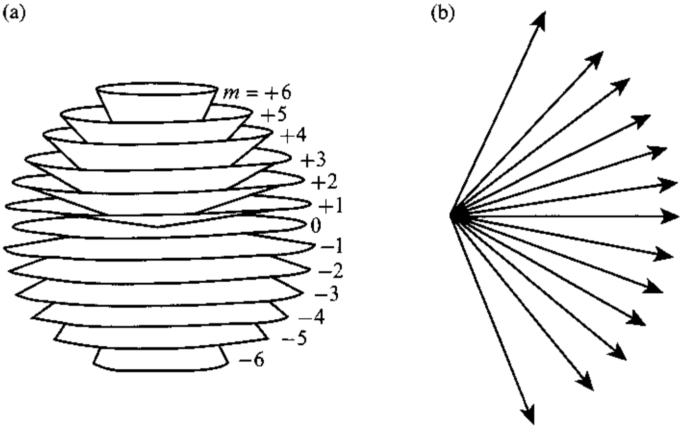

(a) (b)

Figure 8.1(a) & (b)

Solutions to problems

Solutions to numerical problems

8.2 $$\omega = \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2} \quad [8.24]$$

Also, $\omega = 2\pi\nu = \dfrac{2\pi c}{\lambda} = 2\pi c\tilde{\nu}$

Therefore, $k_f = \omega^2 m_{\text{eff}} = 4\pi^2 c^2 \tilde{\nu}^2 m_{\text{eff}} = \dfrac{4\pi^2 c^2 \tilde{\nu}^2 m_1 m_2}{m_1 + m_2}$.

We draw up the following table using isotope masses from the data section:

	$^{1}H^{35}Cl$	$^{1}H^{81}Br$	$^{1}H^{127}I$	$^{12}C^{16}O$	$^{14}N^{16}O$
$\tilde{\nu}/m^{-1}$	299 000	265 000	231 000	217 000	190 400
$10^{27}\, m_1/kg$	1.6735	1.6735	1.6735	19.926	23.253
$10^{27}\, m_2/kg$	58.066	134.36	210.72	26.560	26.560
$k/(N\, m^{-1})$	516	412	314	1902	1595

Therefore, the order of stiffness, is $\boxed{\text{HI} < \text{HBr} < \text{HCl} < \text{NO} < \text{CO}}$.

P8.4

$$E = \frac{l(l+1)\hbar^2}{2I}[8.53] = \frac{l(l+1)\hbar^2}{2\mu R^2} \quad [I = \mu R^2]$$

$$= \left(\frac{l(l+1)\times(1.055\times10^{-34}\,\mathrm{J\,s})^2}{(2)\times(1.6605\times10^{-27}\,\mathrm{kg})\times(160\times10^{-12}\,\mathrm{m})^2}\right)\times\left(\frac{1}{1.008}+\frac{1}{126.90}\right)$$

Therefore,

$$E = l(l+1)\times(1.31\times10^{-22}\,\mathrm{J})$$

The energies may be expressed in terms of equivalent frequencies with

$$\nu = \frac{E}{h} = (1.509\times10^{33}\,\mathrm{J^{-1}\,s^{-1}})E$$

Hence, the energies and equivalent frequencies are

l	0	1	2	3
$10^{22}\,E/\mathrm{J}$	$\boxed{0}$	$\boxed{2.62}$	$\boxed{7.86}$	$\boxed{15.72}$
ν/GHz	0	396	1188	2376

P8.6 Mathematical software can animate the real part or the imaginary part of $\Psi(x,t)$, or you may wish to have it display $|\Psi(x,t)|^2$. Try a 'pure' state, that is, let $c = 1$ for one value of m_l and 0 for all others. This 'packet' does not spread; in fact, $|\Psi(x,t)|^2$ does not change, which is one reason why pure states are sometimes called stationary states. Also, try making all the coefficients in the sum equal (all 1, for example). Whatever your choice of coefficients, the pattern will repeat with a period T that makes all the time-dependent factors equal to the exponential of ($2\pi\mathrm{i}\times$ an integer). Because the energy is

$$E_v = \hbar\omega(v+\tfrac{1}{2}),$$

then, the exponent is equal to $2\pi\mathrm{i}\times$ an integer when

$$\frac{\mathrm{i}E_v t}{\hbar} = \frac{\mathrm{i}\hbar\omega(v+\frac{1}{2})t}{\hbar} = 2\pi\mathrm{i}\times\text{integer}, \quad \text{so} \quad T = \frac{2\pi}{\omega(v+\frac{1}{2})} = \frac{4\pi}{\omega(2v+1)}$$

Thus, a component of the packet returns to its initial value when $t = T$ and at intervals of T thereafter. For a harmonic oscillator, $T = \frac{4\pi}{\omega}$ is the period for the ground state and it is **a** period for any other state (because $\frac{4\pi}{\omega}$ is an integral multiple of $\frac{4\pi}{\omega(2v+1)}$ for all positive integers v.

The following figures show the evolution of a wavepacket composed of the first eleven harmonic oscillator wavefunctions equally weighted. That is, we have set all coefficients equal to 1:

$$\Psi(x,t) = \sum_{v=0}^{10}\psi_v(x)\mathrm{e}^{-\mathrm{i}E_v t/\hbar}$$

Note: The resulting time-dependent wavefunction is not normalized; however, $|\Psi(x,t)|^2$ is proportional to the time-dependent probability of finding the oscillator 'at' (x,t).

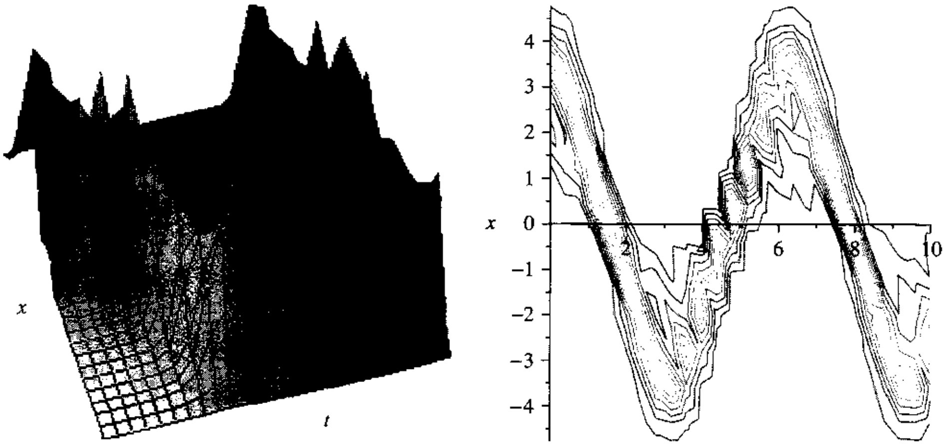


Figure 8.2(a) & (b)

Figure 8.2(a) is a three-dimensional plot of the evolution of $|\Psi(x,t)|^2$ as a function of x and t, and Figure 8.2(b) is a contour plot of the same function. In both plots, x is graphed in units of α (i.e. x is really x/α) and t in units of $1/\omega$ (i.e. t is really ωt). Notice that this wavepacket is fairly localized. At time 0 it is most likely found between $x = 3$ and 4. As the wavepacket moves, it hangs together more or less, that is, its height and breadth do not change by much. Notice that the track repeats itself after a period of t (or rather $\omega t) = 2\pi$.

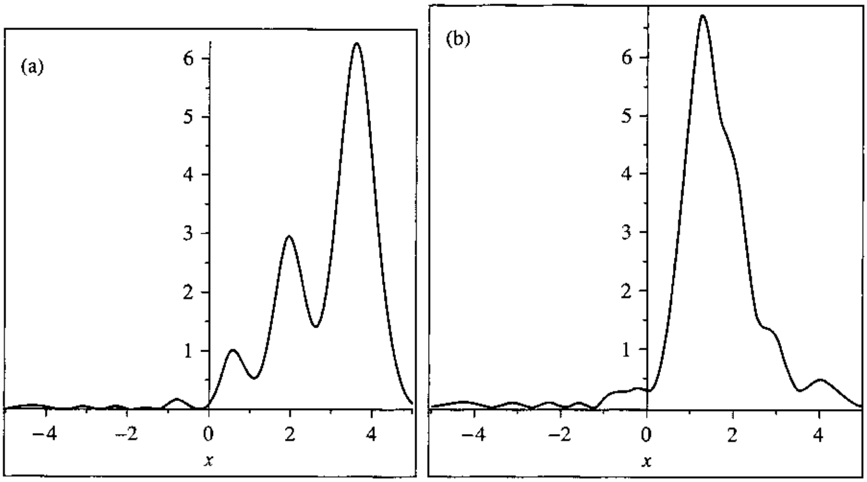


Figure 8.3(a) & (b)

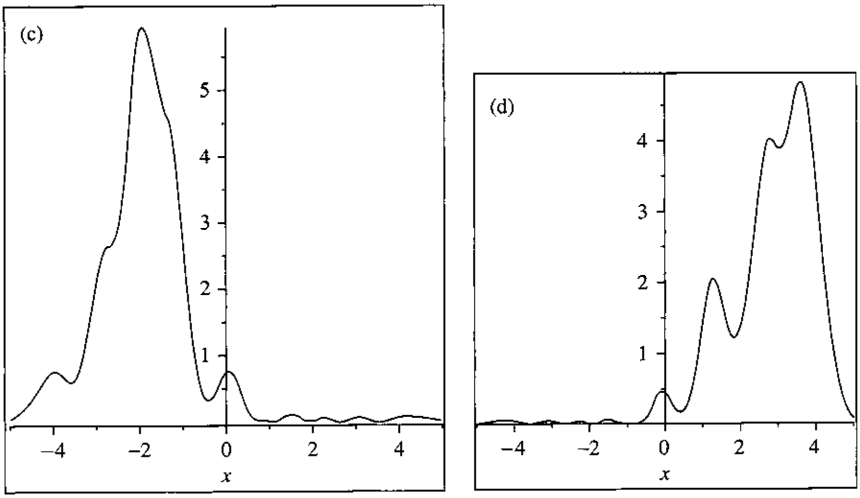


Figure 8.3(c) & (d)

Figures 8.3(a)–(d) show four snapshots of the wavepacket's spatial distribution, at $t = 0, 1, 4$, and 6, during which time we can see that the peak moves across the graph and almost all the way back again.

Solutions to theoretical problems

P8.8 The text defines the transmission probability and expresses it as the ratio of $|A'|^2/|A|^2$, where the coefficients A and A' are introduced in eqns 8.13 and 8.16. Eqns 8.17 and 8.18 list four equations for the six unknown coefficients of the full wavefunction. Once we realize that we can set B' to zero, these equations in five unknowns are:

(a) $A + B = C + D$
(b) $Ce^{\kappa L} + De^{-\kappa L} = A'e^{ikL}$
(c) $ikA - ikB = \kappa C - \kappa D$
(d) $\kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA'e^{ikL}$

We need A' in terms of A alone, which means we must eliminate B, C, and D. Notice that B appears only in eqns (a) and (c). Solving these equations for B and setting the results equal to each other yields:

$$B = C + D - A = A - \frac{\kappa C}{ik} + \frac{\kappa D}{ik}$$

Solve this equation for C:

$$C = \frac{2A + D\left(\dfrac{\kappa}{ik} - 1\right)}{\dfrac{\kappa}{ik} + 1} = \frac{2Aik + D(\kappa - ik)}{\kappa + ik}$$

Now, note that the desired A' appears only in (b) and (d). Solve these for A' and set them equal:

$$A' = e^{-ikL}(Ce^{\kappa L} + De^{-\kappa L}) = \frac{\kappa e^{-ikL}}{ik}(Ce^{\kappa L} - De^{-\kappa L})$$

Solve the resulting equation for C, and set it equal to the previously obtained expression for C:

$$C=\frac{\left(\dfrac{\kappa}{\mathrm{i}k}+1\right)D\mathrm{e}^{-2\kappa L}}{\dfrac{\kappa}{\mathrm{i}k}-1}=\frac{(\kappa+\mathrm{i}k)D\mathrm{e}^{-2\kappa L}}{\kappa-\mathrm{i}k}=\frac{2A\mathrm{i}k+D(\kappa-\mathrm{i}k)}{\kappa+\mathrm{i}k}$$

Solve this resulting equation for D in terms of A:

$$\frac{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L}-(\kappa-\mathrm{i}k)^2}{(\kappa-\mathrm{i}k)(\kappa+\mathrm{i}k)}D=\frac{2A\mathrm{i}k}{\kappa+\mathrm{i}k},$$

$$\text{so}\quad D=\frac{2A\mathrm{i}k(\kappa-\mathrm{i}k)}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L}-(\kappa-\mathrm{i}k)^2}$$

Substituting this expression back into an expression for C yields:

$$C=\frac{2A\mathrm{i}k(\kappa+\mathrm{i}k)\mathrm{e}^{-2\kappa L}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L}-(\kappa-\mathrm{i}k)^2}$$

Substituting for C and D in the expression for A' yields:

$$A'=\mathrm{e}^{-\mathrm{i}kL}(C\mathrm{e}^{\kappa L}+D\mathrm{e}^{-\kappa L})=\frac{2A\mathrm{i}k\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L}-(\kappa-\mathrm{i}k)^2}[(\kappa+\mathrm{i}k)\mathrm{e}^{-\kappa L}+(\kappa-\mathrm{i}k)\mathrm{e}^{-\kappa L}],$$

$$\text{so}\quad \frac{A'}{A}=\frac{4\mathrm{i}k\kappa\mathrm{e}^{-\kappa L}\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L}-(\kappa-\mathrm{i}k)^2}=\frac{4\mathrm{i}k\kappa\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-\kappa L}-(\kappa-\mathrm{i}k)^2\mathrm{e}^{\kappa L}}$$

The transmission probability is:

$$T=\frac{|A'|^2}{|A|^2}=\left(\frac{4\mathrm{i}k\kappa\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-\kappa L}-(\kappa-\mathrm{i}k)^2\mathrm{e}^{\kappa L}}\right)\left(\frac{-4\mathrm{i}k\kappa\mathrm{e}^{\mathrm{i}kL}}{(\kappa-\mathrm{i}k)^2\mathrm{e}^{-\kappa L}-(\kappa+\mathrm{i}k)^2\mathrm{e}^{\kappa L}}\right)$$

The denominator is worth expanding separately in several steps. It is:

$$\begin{aligned}&(\kappa+\mathrm{i}k)^2(\kappa-\mathrm{i}k)^2\mathrm{e}^{-2\kappa L}-(\kappa-\mathrm{i}k)^4-(\kappa+\mathrm{i}k)^4+(\kappa-\mathrm{i}k)^2(\kappa+\mathrm{i}k)^2\mathrm{e}^{2\kappa L}\\&=(\kappa^2+k^2)^2(\mathrm{e}^{2\kappa L}+\mathrm{e}^{-2\kappa L})-(\kappa^2-2\mathrm{i}\kappa k-k^2)^2-(\kappa^2+2\mathrm{i}\kappa k-k^2)^2\\&=(\kappa^4+2\kappa^2k^2+k^4)(\mathrm{e}^{2\kappa L}+\mathrm{e}^{-2\kappa L})-(2\kappa^4-12\kappa^2k^2+2k^4)\end{aligned}$$

If the $12\kappa^2k^2$ term were $-4\kappa^2k^2$ instead, we could collect terms still further (completing the square), but of course we must also account for the difference between those quantities, making the denominator:

$$(\kappa^4+2\kappa^2k^2+k^4)(\mathrm{e}^{2\kappa L}-2+\mathrm{e}^{-2\kappa L})+16\kappa^2k^2=(\kappa^2+k^2)^2(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2+16\kappa^2k^2$$

So the probability is:

$$T=\frac{16k^2\kappa^2}{(\kappa^2+k^2)^2(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2+16\kappa^2k^2}$$

We are almost there. To get to eqn 8.19a, we invert the expression:

$$T=\left(\frac{(\kappa^2+k^2)^2(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2+16\kappa^2k^2}{16k^2\kappa^2}\right)^{-1}=\left(\frac{(\kappa^2+k^2)^2(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2}{16k^2\kappa^2}+1\right)^{-1}$$

Finally, we try to express $\dfrac{(\kappa^2+k^2)^2}{k^2\kappa^2}$ in terms of a ratio of energies, $\varepsilon = E/V$. Eqns 8.13 and 8.15 define k and κ. The factors involving 2, $\hbar$, and the mass cancel, leaving $\kappa \propto (V-E)^{1/2}$ and $\kappa \propto E^{1/2}$, so:

$$\frac{(\kappa^2+k^2)^2}{k^2\kappa^2} = \frac{[E+(V-E)]^2}{E(V-E)} = \frac{V^2}{E(V-E)} = \frac{1}{\varepsilon(1-\varepsilon)},$$

which makes the transmission probability:

$$T = \boxed{\left(\frac{(e^{\kappa L}-e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}+1\right)^{-1}}$$

If $\kappa L \gg 1$, then the negative exponential is negligible compared to the positive, and the 1 inside the parentheses is negligible compared to the exponential:

$$T \approx \left(\frac{e^{2\kappa L}}{16\varepsilon(1-\varepsilon)}\right)^{-1} = \frac{16\varepsilon(1-\varepsilon)}{e^{2\kappa L}} = \boxed{16\varepsilon(1-\varepsilon)e^{-2\kappa L}}$$

P8.10 We assume that the barrier begins at $x = 0$ and extends in the positive x direction.

(a) $$P = \int_{\text{barrier}} \psi^2 d\tau = \int_0^{\infty} N^2 e^{-2\kappa x} dx = \boxed{\frac{N^2}{2\kappa}}$$

(b) $$\langle x\rangle = \int_0^{\infty} x\psi^2 dx = N^2\int_0^{\infty} xe^{-2\kappa x}dx = \frac{N^2}{(2\kappa)^2} = \boxed{\frac{N^2}{4\kappa^2}}$$

Question. Is N a normalization constant?

P8.12
$$\langle E_K\rangle = \int_{-\infty}^{+\infty} \psi^* \hat{E}_K \psi \, dx$$

$$\hat{E}_K = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}[7.31] = -\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{dy^2} = -\frac{\hbar\omega}{2}\frac{d^2}{dy^2}, \quad \left[x = \alpha y, \alpha^2 = \frac{\hbar}{m\omega}\right]$$

which implies that

$$\hat{E}_K\psi = -\frac{\hbar\omega}{2}\left(\frac{d^2\psi}{dy^2}\right)$$

We then use $\psi = NHe^{-y^2/2}$, and obtain

$$\frac{d^2\psi}{dy^2} = N\frac{d^2}{dy^2}(He^{-y^2/2}) = N\{H'' - 2yH' - H + y^2H\}e^{-y^2/2}$$

From Table 8.1

$$H_v'' - 2yH_v' = -2vH_v$$

$$y^2H_v = y(\tfrac{1}{2}H_{v+1} + vH_{v-1}) = \tfrac{1}{2}(\tfrac{1}{2}H_{v+2} + (v+1)H_v) + v(\tfrac{1}{2}H_v + (v-1)H_{v-2})$$
$$= \tfrac{1}{4}H_{v+2} + v(v-1)H_{v-2} + (v+\tfrac{1}{2})H_v$$

Hence, $\dfrac{\mathrm{d}^2\psi}{\mathrm{d}y^2} = N\left[\tfrac{1}{4}H_{v+2} + v(v-1)H_{v-2} - \left(v+\dfrac{1}{2}\right)H_v\right]\mathrm{e}^{-y^2/2}$

Therefore,

$$\langle E_{\mathrm{K}}\rangle = N_v^2\left(-\frac{\hbar\omega}{2}\right)\int_{-\infty}^{+\infty} H_v\left\{\frac{1}{4}H_{v+2} + v(v-1)H_{v-2} - \left(v+\frac{1}{2}\right)H_v\right\}\mathrm{e}^{-y^2}\mathrm{d}x\ [\mathrm{d}x = \alpha\mathrm{d}y]$$

$$= \alpha N_v^2(-\tfrac{1}{2}\hbar\omega)\{0 + 0 - (v+\tfrac{1}{2})\pi^{1/2}2^v v!\}\ \text{[Hermite polynomials orthogonal]}$$

$$= \boxed{\frac{1}{2}\left(v+\frac{1}{2}\right)\hbar\omega}\ \left[N_v^2 = \frac{1}{\alpha\pi^{1/2}2^v v!},\ \text{Example 8.3}\right]$$

P8.14 (a) $\langle x\rangle = \displaystyle\int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)x\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \left(\frac{2}{L}\right)\int_0^L x\sin^2 ax\,\mathrm{d}x\left[a = \frac{n\pi}{L}\right]$

$$= \left(\frac{2}{L}\right)\times\left(\frac{x^2}{4} - \frac{x\sin 2ax}{4a} - \frac{\cos 2ax}{8a^2}\right)\Bigg|_0^L = \left(\frac{2}{L}\right)\times\left(\frac{L^2}{4}\right)$$

$$= \frac{L}{2}\ \text{[by symmetry also]}$$

$$\langle x^2\rangle = \frac{2}{L}\int_0^L x^2\sin^2 ax\,\mathrm{d}x = \left(\frac{2}{L}\right)\times\left[\frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin 2ax - \frac{x\cos 2ax}{4a^2}\right]\Bigg|_0^L$$

$$= \left(\frac{2}{L}\right)\times\left(\frac{L^3}{6} - \frac{L^3}{4n^2\pi^2}\right) = L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

$$\Delta x = \left[L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \frac{L^2}{4}\right]^{1/2} = \boxed{L\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2}}$$

$\langle p\rangle = 0$ [by symmetry, also see Exercise 8.3]

$\langle p^2\rangle = \dfrac{n^2h^2}{4L^2}$ [from $E = \dfrac{p^2}{2m}$, also Exercise 8.3(b)]

$$\Delta p = \left(\frac{n^2h^2}{4L^2}\right)^{1/2} = \boxed{\frac{nh}{2L}}$$

$$\Delta p\Delta x = \frac{nh}{2L}\times L\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2} = \frac{nh}{2\sqrt{3}}\left(1 - \frac{1}{24\pi^2 n^2}\right)^{1/2} > \frac{\hbar}{2}$$

(b) $\langle x\rangle = 0$ [8.32, or by symmetry]

and $\langle x^2\rangle = \left(v+\dfrac{1}{2}\right)\times\left(\dfrac{\hbar^2}{mk_{\mathrm{f}}}\right)^{1/2}$ [8.32] $= \left(v+\dfrac{1}{2}\right)\times\left(\dfrac{\hbar}{\omega m}\right)$ [8.24] so $$\Delta x = \boxed{\left\{\left(v+\frac{1}{2}\right)\frac{\hbar}{\omega m}\right\}^{1/2}}$$

$\langle p\rangle = 0$ [by symmetry, or by noting that the integrand is an odd function of x]

and $$\langle p^2\rangle = 2m\langle E_{\mathrm{K}}\rangle = (2m)\times\left(\frac{1}{2}\right)\times\left(v+\frac{1}{2}\right)\times\hbar\omega \text{ [Problem 8.12]}$$

so $$\Delta p = \boxed{\left\{\left(v+\frac{1}{2}\right)\hbar\omega m\right\}^{1/2}}$$

$$\Delta p\Delta x = \left(v+\frac{1}{2}\right)\hbar \geq \frac{\hbar}{2}$$

COMMENT. Both results show a consistency with the uncertainty principle in the form $\Delta p\Delta q \geq \dfrac{\hbar}{2}$ as given in Section 7.6, eqn 7.39a.

P8.16 The turning points in terms of the displacement x are

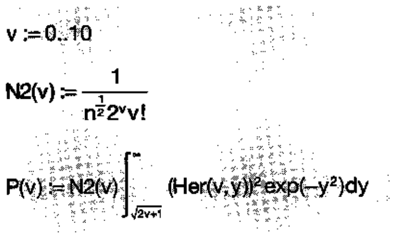
$$x_{\mathrm{tp}} = \pm\left(\frac{2E}{k}\right)^{1/2} = \pm\left(\frac{2(v+\frac{1}{2})\hbar\omega}{k}\right)^{1/2} = \pm\left(\frac{(2v+1)\hbar}{(km)^{1/2}}\right)^{1/2} \text{ [8.24]} = \pm(2v+1)^{1/2}\alpha \text{ [8.27]}$$

In terms of the dimensionless variable $y = x/\alpha$, $y_{\mathrm{tp}} = \pm(2v+1)^{1/2}$.

The probability of extension beyond one classical turning point for a harmonic oscillator with quantum number v is

$$P_v = \int_{|x_{\mathrm{tp}}|}^{\infty}\psi_v^2\,\mathrm{d}x = \alpha N_v^2\int_{(2v+1)^{1/2}}^{\infty}\{H_v(y)\}^2\mathrm{e}^{-y^2}\mathrm{d}y = \frac{1}{\pi^{1/2}2^v v!}\int_{(2v+1)^{1/2}}^{\infty}\{H_v(y)\}^2\mathrm{e}^{-y^2}\mathrm{d}y$$

This expression can be evaluated for an arbitrary integer v. Mathematical software packages such as Maple, Mathcad, and Mathematica have the Hermite polynomials built in, so the above expression can be entered in a relatively straightforward manner. Here is what it looks like in Mathcad:



$$\mathrm{v} := 0..10$$

$$\mathrm{N2(v)} := \frac{1}{\mathrm{n}^{\frac{1}{2}}2^{\mathrm{v}}\mathrm{v!}}$$

$$\mathrm{P(v)} := \mathrm{N2(v)}\int_{\sqrt{2\mathrm{v}+1}}^{\infty}(\mathrm{Her(v,y)})^2\exp(-\mathrm{y}^2)\mathrm{dy}$$

The table of results is

v	0	1	2	3	4	5	6	7	8	9	10
$P(v)$ %	7.90	5.61	4.79	4.31	3.98	3.73	3.54	3.38	3.25	3.14	3.04

where $P(v)$ is expressed as a percentage (i.e. as $P(v)/100$).

The points are plotted (as probabilities, not percentages) in Figure 8.4.

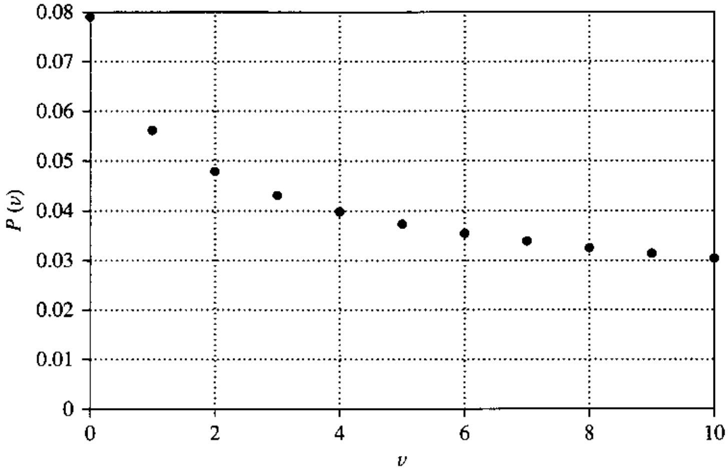


Figure 8.4

COMMENT. *P*(*v*) decreases with increasing *v*, albeit very slowly after the first few states. According to the correspondence principle, the quantum result reduces to the classical result in the limit of very high quantum numbers. So, the probability of finding a displacement beyond the classical turning point must vanish in the limit of very high *v*.

P8.18 As expressed in the problem, the potential energy function assumes that ϕ is defined as we would expect; that is, $\phi = 0$ corresponds to an eclipsed conformation. Thus, $\phi = 0$ is *not* a stable equilibrium point, and small displacements from this point are *not* harmonic; in fact, $\phi = 0$ is a position of unstable equilibrium, and small displacements from it would grow larger. We must express the potential energy in terms of displacements from a stable equilibrium position. One such equilibrium position is the staggered conformation directly opposite $\phi = 0$, namely $\phi = \pi$. So, let the displacement $x = \phi - \pi$. In terms of x, the potential energy function is $V = -V_0 \cos 3x$. Conventionally, the potential energy in harmonic motion is measured with respect to that stable equilibrium position. Note that the potential energy at the stable equilibrium position is $V = -V_0$. We can redefine the potential energy function to measure energy relative to the stable equilibrium by letting

$$V' = V_0 + V = V_0 - V_0 \cos 3x = V_0(1 - \cos 3x).$$

Use the first two terms of the Taylor series expansion of cosine:

$$V' = V_0(1 - \cos 3x) \approx V_0\left(1 - 1 + \frac{(3x)^2}{2}\right) = \frac{9V_0}{2}x^2$$

The Schrödinger equation becomes

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial x^2} + \frac{9V_0}{2}x^2\psi = E\psi \text{ [8.40 with a non-zero potential energy]}$$

This has the form of the Schrödinger equation for the harmonic oscillator wavefunction (eqn 8.23). The difference in adjacent energy levels is:

$$E_1 - E_0 = \hbar\omega \text{ [8.25]}, \quad \text{where} \quad \omega = \left(\frac{9V_0}{I}\right)^{1/2} \text{ [adapting 8.24]}$$

If the displacements are sufficiently large, the potential energy does not rise as rapidly with the angle as would a harmonic potential (i.e. the cosine potential energy is not well approximated by the first few terms of its expansion). Each successive energy level would become lower than that of a harmonic oscillator, so the energy levels would become progressively closer together.

Question. The next term in the Taylor series for the potential energy is $-\frac{27V_0}{8}x^4$. Treat this as a perturbation to the harmonic oscillator wavefunction and compute the first-order correction to the energy.

P8.20 $$V=-\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}\,[9.4\text{ with }Z=1]=\alpha x^b \quad \text{with } b=-1\,[x\to r]$$

Since $2\langle E_K\rangle=b\langle V\rangle$ [virial theorem, 8.35] $=-\langle V\rangle$ [virial theorem, 8.35]

Therefore, $\langle E_K\rangle=\boxed{-\frac{1}{2}\langle V\rangle}$

P8.22 The elliptical ring to which the particle is confined is defined by the set of all points that obey a certain equation. In Cartesian coordinates, that equation is

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}=1$$

as you may remember from analytical geometry. An ellipse is similar to a circle, and an appropriate change of variable can transform the ellipse of this problem into a circle. That change of variable is most conveniently described in terms of new Cartesian coordinates (X,Y) where

$$X=x \quad \text{and} \quad Y=ay/b$$

In this new coordinate system, the equation for the ellipse becomes:

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}=1 \quad\Rightarrow\quad \frac{X^2}{a^2}+\frac{Y^2}{a^2}=1 \quad\Rightarrow\quad X^2+Y^2=a^2,$$

which we recognize as the equation of a circle of radius a centered at the origin of our (X,Y) system. The text found the eigenfunctions and eigenvalues for a particle on a circular ring by transforming from Cartesian coordinates to plane polar coordinates. Consider plane polar coordinates (R,Φ) related in the usual way to (X,Y):

$$X=R\cos\Phi \quad \text{and} \quad Y=R\sin\Phi$$

In this coordinate system, we can simply quote the results obtained in the text. The energy levels are

$$E=\frac{m_l^2\hbar^2}{2I}\ [8.38\text{a}]$$

where the moment of inertia is the mass of the particle times the radius of the circular ring

$$I=ma^2$$

The eigenfunctions are

$$\psi=\frac{e^{im_l\Phi}}{(2\pi)^{1/2}}\ [8.38\text{b}]$$

It is customary to express results in terms of the original coordinate system, so express Φ in the wavefunction in terms first of X and Y, and then substitute the original coordinates:

$$\frac{Y}{X}=\tan\Phi, \quad \text{so} \quad \Phi=\tan^{-1}\frac{Y}{X}=\tan^{-1}\frac{ay}{bx}$$

P8.24 Call the integral I:

$$I=\int_0^{\pi}\int_0^{2\pi} Y_{3,3}^{*}Y_{3,3}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=\left(\frac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\int_0^{\pi}\sin^6\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi \text{ [Table 8.2]}$$

Integration over $\mathrm{d}\phi$ yields a factor of 2π. Noting that $\sin\theta\,\mathrm{d}\theta=\mathrm{d}\cos\theta$, and that $\sin^2\theta=1-\cos^2\theta$, the integral becomes

$$I=\left(\frac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\times(2\pi)\int_{-1}^{1}(1-\cos^2\theta)^3\,\mathrm{d}\cos\theta$$

Letting $x=\cos\theta$ and expanding the integrand, we have

$$I=\frac{35}{32}\int_{-1}^{1}(1-3x^2+3x^4-x^6)\mathrm{d}x=\frac{35}{32}\left(x-x^3+\tfrac{3}{5}x^5-\tfrac{1}{7}x^7\right)\Big|_{-1}^{1}=\frac{35}{32}\times\frac{32}{35}=\boxed{1}$$

P8.26

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \text{ [Table 7.1]}$$

$$\frac{\partial^2}{\partial x^2}f=-a^2\cos ax\cos by\cos cz=-a^2f$$

Similarly, $\dfrac{\partial^2}{\partial y^2}f=-b^2f \quad \dfrac{\partial^2}{\partial y^2}f=-c^2f$

so f is an eigenfunction with eigenvalue $\boxed{-(a^2+b^2+c^2)}$.

P8.28 On making the operator substitutions

$$p_x=\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x} \text{ and } p_y=\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial y}$$

into $\hat{l}_z$ we find

$$\hat{l}_z=\frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$$

But $\dfrac{\partial}{\partial\phi}=\dfrac{\partial x}{\partial\phi}\dfrac{\partial}{\partial x}+\dfrac{\partial y}{\partial\phi}\dfrac{\partial}{\partial y}+\dfrac{\partial z}{\partial\phi}\dfrac{\partial}{\partial z}$ [chain rule of partial differentiation]

$$\frac{\partial x}{\partial\phi}=\frac{\partial}{\partial\phi}(r\sin\theta\cos\phi)=-r\sin\theta\sin\phi=-y$$

$$\frac{\partial y}{\partial \phi} = \frac{\partial}{\partial \phi}(r\sin\theta\sin\phi) = r\sin\theta\cos\phi = x$$

$$\frac{\partial z}{\partial \phi} = 0$$

Thus, $\dfrac{\partial}{\partial \phi} = -y\dfrac{\partial}{\partial x} + x\dfrac{\partial}{\partial y}$

On substitution,

$$\hat{l}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \phi} = -\mathrm{i}\hbar\frac{\partial}{\partial \phi}$$

P8.30 (a) Suppose that a particle moves classically at the constant speed v. It starts at $x = 0$ at $t = 0$ and at $t = \tau$ is at position $x = L$. $v = \dfrac{L}{\tau}$ and $x = vt$.

$$\langle x\rangle = \frac{1}{\tau}\int_{t=0}^{\tau} x\,\mathrm{d}t = \frac{1}{\tau}\int_{t=0}^{\tau} vt\,\mathrm{d}t = \frac{v}{\tau}\int_{t=0}^{\tau} t\,\mathrm{d}t = \frac{v}{2\tau}t^2\Big|_{t=0}^{\tau} = \frac{v\tau^2}{2\tau} = \frac{v\tau}{2} = \boxed{\frac{L}{2}}$$

$$\langle x^2\rangle = \frac{1}{\tau}\int_{t=0}^{\tau} x^2\,\mathrm{d}t = \frac{v^2}{\tau}\int_{t=0}^{\tau} t^2\,\mathrm{d}t = \frac{v^2}{3\tau}t^3\Big|_{t=0}^{\tau} = \frac{(v\tau)^2}{3} = \frac{L^2}{3}$$

so $\langle x^2\rangle^{1/2} = \boxed{\dfrac{L}{3^{1/2}}}$

(b) $\psi_n = \left(\dfrac{2}{L}\right)^{1/2}\sin\left(\dfrac{n\pi x}{L}\right)$ for $0 \le x \le L$ [8.4b]

$$\langle x\rangle_n = \int_{x=0}^{L} \psi_n^* x\psi_n\,\mathrm{d}x = \frac{2}{L}\int_0^L x\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$= \frac{2}{L}\left\{\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi x}{L}\right)}{4(n\pi/L)} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right\}\Bigg|_{x=0}^{x=L} = \frac{2}{L}\left(\frac{L^2}{4}\right) = \boxed{\frac{L}{2}}$$

This agrees with the classical result for all values of n.

$$\langle x^2\rangle_n = \int_{x=0}^{L} \psi_n^* x^2\psi_n\,\mathrm{d}x = \frac{2}{L}\int_{x=0}^{L} x^2\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$= \frac{2}{L}\left\{\frac{x^3}{6} - \left(\frac{x^2}{4(n\pi/L)} - \frac{1}{8(n\pi/L)^3}\right)\sin\left(\frac{2n\pi x}{L}\right) - \frac{x\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right\}\Bigg|_{x=0}^{x=L}$$

$$= \frac{2}{L}\left(\frac{L^3}{6} - \frac{L}{8(n\pi/L)^2}\right) = \frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}$$

so $$\langle x^2\rangle_n^{1/2} = \boxed{\left(\frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}\right)^{1/2}}$$

This agrees with the classical result in the limit of large quantum numbers:

$$\lim_{n\to\infty}\langle x^2\rangle_n^{1/2} = \frac{L}{3^{1/2}}$$

Solutions to applications

P8.32 The rate of tunnelling is proportional to the transmission probability, so a ratio of tunnelling rates is equal to the corresponding ratio of transmission probabilities (given in eqn 8.19a). The desired factor is T_1/T_2, where the subscripts denote the tunnelling distances in nanometres:

$$\frac{T_1}{T_2} = \frac{1 + \dfrac{(\mathrm{e}^{\kappa L_2} - \mathrm{e}^{-\kappa L_2})^2}{16\varepsilon(1-\varepsilon)}}{1 + \dfrac{(\mathrm{e}^{\kappa L_1} - \mathrm{e}^{-\kappa L_1})^2}{16\varepsilon(1-\varepsilon)}}.$$

If $$\frac{(\mathrm{e}^{\kappa L_2} - \mathrm{e}^{-\kappa L_2})^2}{16\varepsilon(1-\varepsilon)} \gg 1,$$

then $$\frac{T_1}{T_2} \approx \frac{(\mathrm{e}^{\kappa L_2} - \mathrm{e}^{-\kappa L_2})^2}{(\mathrm{e}^{\kappa L_1} - \mathrm{e}^{-\kappa L_1})^2} \approx \mathrm{e}^{2\kappa(L_2-L_1)} = \mathrm{e}^{2(7/\mathrm{nm})(2.0-1.0)\mathrm{nm}} = \boxed{1.2\times10^6}$$

That is, the tunnelling rate increases about a million-fold.

Note: If the first approximation does not hold, we need more information, namely $\varepsilon = E/V$. If the first approximation is valid, then the second is also likely to be valid, namely that the negative exponential is negligible compared to the positive one.

P8.34 Assuming that one can identify the CO peak in the infrared spectrum of the CO-myoglobin complex, taking infrared spectra of each of the isotopic variants of CO-myoglobin complexes can show which atom binds to the haem group and determine the C≡O force constant. Compare isotopic variants to $^{12}C^{16}O$ as the standard; when an isotope changes but the vibrational frequency does not, then the atom whose isotope was varied is the atom that binds to the haem. See the table below, which includes predictions of the wavenumber of all isotopic variants compared to that of $\tilde{\nu}$ ($^{12}C^{16}O$). (As usual, the better the experimental results agree with the whole set of predictions, the more confidence one would have with the conclusion.)

Wavenumber for isotopic variant	If O binds	If C binds
$\tilde{\nu}(^{12}C^{18}O) =$	$\tilde{\nu}(^{12}C^{16}O)$†	$(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$
$\tilde{\nu}(^{13}C^{16}O) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$	$\tilde{\nu}(^{12}C^{16}O)$†
$\tilde{\nu}(^{13}C^{18}O) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$	$(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$

†That is, no change compared to the standard.

The wavenumber is related to the force constant as follows:

$$\omega = 2\pi c\tilde{\nu} = \left(\frac{k_f}{m}\right)^{1/2}, \quad \text{so} \quad k_f = m(2\pi c\tilde{\nu})^2$$

Hence, $k_f = (m/m_u)(1.66\times10^{-27}\ \text{kg})[(2\pi)(2.998\times10^{10}\ \text{cm s}^{-1})\tilde{\nu}(^{12}\text{C}^{16}\text{O})]^2$,

and $k_f/(\text{kg s}^{-1}) = (5.89\times10^{-5})(m/m_u)[\tilde{\nu}(^{12}\text{C}^{16}\text{O})/\text{cm}^{-1}]^2$

Here, m is the mass of the atom that is not bound in atomic mass units, i.e. $12m_u$ if O is bound and $16m_u$ if C is bound. (Of course, one can compute k_f from any of the isotopic variants, and take k_f to be a mean derived from all the relevant data.)

P8.36 First, let $f = n/N$, therefore f is the fraction of the totally stretched chain represented by the end-to-end distance.

$$F = -\frac{kT}{2l}\ln\left(\frac{N+n}{N-n}\right) = -\frac{kT}{2l}\ln\left(\frac{N(1+f)}{N(1-f)}\right) = -\frac{kT}{2l}\ln\left(\frac{1+f}{1-f}\right)$$
$$= -\frac{kT}{2l}[\ln(1+f) - \ln(1-f)]$$

When $n \ll N$, then $f \ll 1$, and the natural log can be expanded: $\ln(1+f) \approx f$ and $\ln(1-f) \approx -f$. Therefore,

$$F \approx -\frac{kT}{2l}[f-(-f)] = -\frac{fkT}{l} = -\frac{nkT}{Nl} = -\frac{kT}{Nl^2}x$$

In the last step, we note that the distance x between ends is equal to nl, so $n = x/l$. This is a Hooke's law force with force constant kT/Nl^2.

The root mean square displacement is $\langle x^2\rangle^{1/2}$. For a harmonic oscillator

$$\langle x^2\rangle = \left(v+\frac{1}{2}\right)\times\left(\frac{\hbar^2}{mk_f}\right)^{1/2} \quad [8.32]$$

Therefore, putting in the appropriate values for the ground state ($v = 0$) of this model

$$\langle x^2\rangle = \frac{1}{2}\times\left(\frac{\hbar^2}{m}\times\frac{Nl^2}{kT}\right)^{1/2} = \frac{\hbar l}{2}\times\left(\frac{N}{mkT}\right)^{1/2}$$

and $\langle x^2\rangle^{1/2} = \boxed{\left(\frac{\hbar l}{2}\right)^{1/2}\times\left(\frac{N}{mkT}\right)^{1/4}}$

P8.38 (a) In the sphere, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2\right)\psi = E\psi \quad [8.49 \text{ and } 8.51\text{a}]$$

where Λ^2 is an operator that contains derivatives with respect to θ and ϕ only.

Let $\psi(r,\theta,\phi) = u(r)\,Y(\theta,\phi)$

Substituting into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m}\left(Y\frac{\partial^2 u}{\partial r^2}+\frac{2Y}{r}\frac{\partial u}{\partial r}+\frac{u}{r^2}\Lambda^2 Y\right)=EuY$$

Divide both sides by uY:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2}{ur}\frac{\partial u}{\partial r}+\frac{1}{Yr^2}\Lambda^2 Y\right)=E$$

The first two terms in parentheses depend only on r, but the last one depends on both r and angles; however, multiplying both sides of the equation by r^2 will effect the desired separation:

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2r}{u}\frac{\partial u}{\partial r}+\frac{1}{Y}\Lambda^2 Y\right)=Er^2$$

Put all of the terms involving angles on the right-hand side and the terms involving distance on the left:

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2r}{u}\frac{\partial u}{\partial r}\right)-Er^2=\frac{\hbar^2}{2mY}\Lambda^2 Y$$

Note that the right side depends only on θ and ϕ, while the left side depends only on r. The two sides can be equal to each other for all r,θ, and ϕ only if they are both equal to a constant. Call that constant $-\frac{\hbar^2 l(l+1)}{2m}$ (with l as yet undefined) and we have, from the right side of the equation:

$$\frac{\hbar^2}{2mY}\Lambda^2 Y=-\frac{\hbar^2 l(l+1)}{2m}, \quad \text{so} \quad \Lambda^2 Y=-l(l+1)Y$$

From the left side of the equation, we have

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2r}{u}\frac{\partial u}{\partial r}\right)-Er^2=-\frac{\hbar^2 l(l+1)}{2m}$$

After multiplying both sides by u/r^2 and rearranging, we get the desired radial equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 u}{\partial r^2}+\frac{2}{r}\frac{\partial u}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2mr^2}u=Eu$$

Thus, the assumption that the wavefunction can be written as a product of functions is a valid one, for we can find separate differential equations for the assumed factors. That is what it means for a partial differential equation to be separable.

(b) The radial equation with $l = 0$ can be rearranged to read:

$$\frac{\partial^2 u}{\partial r^2}+\frac{2}{r}\frac{\partial u}{\partial r}=-\frac{2mEu}{\hbar^2}$$

Form the following derivatives of the proposed solution:

$$\frac{\partial u}{\partial r} = (2\pi R)^{-1/2}\left\{\frac{\cos(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right) - \frac{\sin(n\pi r/R)}{r^2}\right\}$$

and $$\frac{\partial^2 u}{\partial r^2} = (2\pi R)^{-1/2}\left\{-\frac{\sin(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right)^2 - \frac{2\cos(n\pi r/R)}{r^2}\left(\frac{n\pi}{R}\right) + \frac{2\sin(n\pi r/R)}{r^3}\right\}$$

Substituting into the left side of the rearranged radial equation yields

$$(2\pi R)^{-1/2}\left[-\frac{\sin(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right)^2 - \frac{2\cos(n\pi r/R)}{r^2}\left(\frac{n\pi}{R}\right) + \frac{2\sin(n\pi r/R)}{r^3}\right]$$

$$+ (2\pi R)^{-1/2}\left[\frac{2\cos(n\pi r/R)}{r^2}\left(\frac{n\pi}{R}\right) - \frac{2\sin(n\pi r/R)}{r^3}\right]$$

$$= -(2\pi R)^{-1/2}\frac{\sin(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right)^2 = -\left(\frac{n\pi}{R}\right)^2 u$$

Acting on the proposed solution by taking the prescribed derivatives yields the function back multiplied by a constant, so the proposed solution is in fact a solution.

(c) Comparing this result to the right side of the rearranged radial equation gives an equation for the energy

$$\left(\frac{n\pi}{R}\right)^2 = \frac{2mE}{\hbar^2}, \quad \text{so} \quad E = \left(\frac{n\pi}{R}\right)^2 \frac{\hbar^2}{2m} = \frac{n^2\pi^2}{2mR^2}\left(\frac{h}{2\pi}\right)^2 = \frac{n^2h^2}{8mR^2}$$

9 Atomic structure and atomic spectra

Answers to discussion questions

D9.2 The Schrödinger equation for the hydrogen atom is a six-dimensional partial differential equation, three dimensions for each particle in the atom. One cannot directly solve a multidimensional differential equation; it must be broken down into one-dimensional equations. This is the separation of variables procedure. The choice of coordinates is critical in this process. The separation of the Schrödinger equation can be accomplished in a set of coordinates that are natural to the system, but not in others. These natural coordinates are those directly related to the description of the motion of the atom. The atom as a whole (centre of mass) can move from point to point in three-dimensional space. The natural coordinates for this kind of motion are the Cartesian coordinates of a point in space. The internal motion of the electron with respect to the proton is most naturally described with spherical polar coordinates. So, the six-dimensional Schrödinger equation is first separated into two three-dimensional equations, one for the motion of the centre of mass, the other for the internal motion. The separation of the centre of mass equation and its solution is fully discussed in Section 8.2. The equation for the internal motion is separable into three one-dimensional equations, one in the angle ϕ, another in the angle θ, and a third in the distance r. The solutions of these three one-dimensional equations can be obtained by standard techniques and were already well known long before the advent of quantum mechanics. Another choice of coordinates would not have resulted in the separation of the Schrödinger equation just described. For the details of the separation procedure, see Sections 9.1a and 8.7.

D9.4 The selection rules are:

$$\Delta n = \pm1, \pm2, \ldots \quad \Delta l = \pm1 \quad \Delta m_l = 0, \pm1$$

In a spectroscopic transition the atom emits or absorbs a photon. Photons have a spin angular momentum of 1, therefore as a result of the transition the angular momentum of the electromagnetic field has changed by $\pm 1\hbar$. The principle of the conservation of angular momentum then requires that the angular momentum of the atom has undergone an equal and opposite change in angular momentum, hence the selection rule on $\Delta l = \pm1$. The principle quantum number n can change by any amount since n does not directly relate to angular momentum. The selection rule on Δm_1 is harder to account for on the basis of these simple considerations alone. One has to evaluate the transition dipole moment between the wavefunctions representing the initial and final states involved in the transition. See *Justification* 9.4 for an example of this procedure.

D9.6 See Section 9.4(d) of the text and any general chemistry book, for example Sections 1.10–1.13 of P. Atkins and L. Jones, *Chemical Principles*, 2nd edn, W. H. Freeman, and Co., New York (2002).

D9.8 In the crudest form of the orbital approximation, the many-electron wavefunctions for atoms are represented as a simple product of one-electron wavefunctions. At a somewhat more sophisticated level, the many-electron wavefunctions are written as linear combinations of such simple product functions that explicitly satisfy the Pauli exclusion principle. Relatively good one-electron functions are generated by the Hartree–Fock self-consistent field method described in Section 9.5. If we place no restrictions on the form of the one-electron functions, we reach the Hartree–Fock limit, which gives us the best value of the calculated energy within the orbital approximation. The orbital approximation is based on the disregard of significant portions of the electron–electron interaction terms in the many-electron Hamiltonian, so we cannot expect that it will be quantitatively accurate. By abandoning the orbital approximation, we could in principle obtain essentially exact energies; however, there are significant conceptual advantages to retaining the orbital approximation. Increased accuracy can be obtained by reintroducing the neglected electron–electron interaction terms and including their effects on the energies of the atom.

D9.10 (1) *Doppler broadening.* This contribution to the linewidth is due to the Doppler effect, which shifts the frequency of the radiation emitted or absorbed when the atoms or molecules involved are moving towards or away from the detecting device. Molecules have a wide range of speeds in all directions in a gas and the detected spectral line is the absorption or emission profile arising from all the resulting Doppler shifts. As shown in *Justification* 9.8, the profile reflects the distribution of molecular velocities parallel to the line of sight, which is a bell-shaped Gaussian curve.

(2) *Lifetime broadening.* The Doppler broadening is significant in gas-phase samples, but lifetime broadening occurs in all states of matter. This kind of broadening is a quantum-mechanical effect related to the uncertainty principle in the form of eqn 9.39 and is due to the finite lifetimes of the states involved in the transition. When τ is finite, the energy of the states is smeared out and hence the transition frequency is broadened, as shown in the *Brief Illustration* in Section 9.6(b).

(3) *Pressure broadening or collisional broadening.* The actual mechanism affecting the lifetime of energy states depends on various processes, one of which is collisional deactivation and another is spontaneous emission. Lowering the pressure can reduce the first of these contributions; the second cannot be changed and results in a natural linewidth.

Doppler broadening and pressure broadening are expected to be of significance only in the gas phase, but in condensed phases there are other kinds of interactions that exist because of the closeness of the species to each other that can result in the broadening of spectral lines.

Solutions to exercises

E9.1(b) Eqn 9.1 implies that the shortest wavelength corresponds to $n_2 = \infty$, and the longest to $n_2 = 6$. Solve eqn 9.1 for λ:

$$\lambda = \frac{(1/n_1^2 - 1/n_2^2)^{-1}}{\tilde{R}_H}$$

Shortest: $\lambda = \dfrac{(1/5^2 - 1/\infty^2)^{-1}}{109\,677\ \mathrm{cm^{-1}}} = 2.279 \times 10^{-4}\ \mathrm{cm}$

Longest: $\lambda = \dfrac{(1/5^2 - 1/6^2)^{-1}}{109\,677\ \mathrm{cm^{-1}}} = 7.460 \times 10^{-4}\ \mathrm{cm}$

9.2(b) For atoms A, eqn 9.9 may be rewritten in terms of the Rydberg constant R_A as

$$E_n = -\frac{Z^2\mu_A hcR_A}{m_e n^2} \approx -\frac{Z^2hcR_\infty}{n^2}$$

where to within 0.01% the ratio μ_A/m_e is unity. Eqn 9.1 can then be rewritten as

$$\tilde{\nu} = Z^2R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \lambda = \frac{1}{\tilde{\nu}} \quad \nu = \frac{c}{\lambda}$$

$$\tilde{\nu} = 9 \times 109\,737\ \text{cm}^{-1}\left(\frac{1}{4^2} - \frac{1}{5^2}\right) = \boxed{2.222 \times 10^4\ \text{cm}^{-1}} \qquad \lambda = \boxed{4.500 \times 10^{-5}\ \text{cm}}$$

$$\nu = \frac{2.9978 \times 10^{10}\ \text{cm s}^{-1}}{4.500 \times 10^{-5}\ \text{cm}} = \boxed{6.662 \times 10^{14}\ \text{s}^{-1}}$$

E9.3(b) The energy of the photon that struck the Xe atom goes into liberating the bound electron and giving it any kinetic energy it now possesses

$$E_{\text{photon}} = I + E_{\text{kinetic}} \qquad I = \text{ionization energy}$$

The energy of a photon is related to its frequency and wavelength

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

and the kinetic energy of an electron is related to its mass and speed, s

$$E_{\text{kinetic}} = \tfrac{1}{2}m_e s^2$$

So, $\dfrac{hc}{\lambda} = I + \tfrac{1}{2}m_e s^2 \Rightarrow I = \dfrac{hc}{\lambda} - \tfrac{1}{2}m_e s^2$

$$I = \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1})}{58.4 \times 10^{-9}\ \text{m}} - \tfrac{1}{2}(9.11 \times 10^{-31}\ \text{kg}) \times (1.79 \times 10^6\ \text{m s}^{-1})^2$$

$$= \boxed{1.94 \times 10^{-18}\ \text{J}}$$

$$= 12.1\ \text{eV}$$

E9.4(b) The degeneracy g of a hydrogenic atom with principal quantum number n is $g = n^2$. The energy E of hydrogenic atoms is

$$E = -\frac{hcZ^2R_{\text{Atom}}}{n^2}$$

$$= -\frac{hcZ^2R_{\text{Atom}}}{g}$$

so the degeneracy is

$$g = -\frac{hcZ^2R_{\text{Atom}}}{E}$$

(a) $g = -\dfrac{hc(2)^2 R_{\text{Atom}}}{-4hcR_{\text{Atom}}} = \boxed{1}$

(b) $g = -\dfrac{hc(4)^2 R_{\text{Atom}}}{-\frac{1}{4}hcR_{\text{Atom}}} = \boxed{64}$

(c) $g = -\dfrac{hc(5)^2 R_{\text{Atom}}}{-hcR_{\text{Atom}}} = \boxed{25}$

E9.5(b) Normalization requires

$$\int |\psi|^2 \,\mathrm{d}\tau = 1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} [N(2 - r/a_0)\mathrm{e}^{-r/2a_0}]^2 \,\mathrm{d}\phi \sin\theta \,\mathrm{d}\theta\, r^2 \,\mathrm{d}r$$

$$1 = N^2 \int_0^\infty \mathrm{e}^{-r/a_0}(2 - r/a_0)^2 r^2 \,\mathrm{d}r \int_0^\pi \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$

Integrating over angles yields

$$1 = 4\pi N^2 \int_0^\infty \mathrm{e}^{-r/a_0}(2 - r/a_0)^2 r^2 \,\mathrm{d}r$$

$$= 4\pi N^2 \int_0^\infty \mathrm{e}^{-r/a_0}(4 - 4r/a_0 + r^2/a_0^2) r^2 \,\mathrm{d}r = 4\pi N^2 (8a_0^3)$$

In the last step, we used $\int_0^\infty \mathrm{e}^{-r/k} r^2 \,\mathrm{d}r = 2k^3$, $\int_0^\infty \mathrm{e}^{-r/k} r^3 \,\mathrm{d}r = 6k^4$, and $\int_0^\infty \mathrm{e}^{-r/k} r^4 \,\mathrm{d}r = 24k^5$,

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

E9.6(b) The radial wavefunction is [Table 9.1]

$R_{3,0} = A(6 - 2\rho + \frac{1}{9}\rho^2)\mathrm{e}^{-\rho/6}$, where $\rho \equiv \dfrac{2Zr}{a_0}$, and A is a collection of constants.

(**Note:** ρ defined here is $3 \times \rho$ as defined in Table 9.1.)

Differentiating with respect to ρ yields

$$\frac{\mathrm{d}R_{3,0}}{\mathrm{d}\rho} = 0 = A(6 - 2\rho + \tfrac{1}{9}\rho^2) \times (-\tfrac{1}{6})\mathrm{e}^{-\rho/6} + (-2 + \tfrac{2}{9}\rho)A\mathrm{e}^{-\rho/6}$$
$$= A\mathrm{e}^{-\rho/6}(-\tfrac{\rho^2}{54} + \tfrac{5}{9}\rho - 3)$$

This is a quadratic equation

$$0 = a\rho^2 + b\rho + c, \quad \text{where} \quad a = -\frac{1}{54},\ b = \frac{5}{9},\ \text{and } c = -3.$$

The solution is

$$\rho = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = 15 \pm 3\sqrt{7}$$

$$\text{so } r = \boxed{\left(\frac{15}{2} \pm \frac{3(7^{1/2})}{2}\right)\frac{a_0}{Z}}.$$

Numerically, this works out to $\rho = 22.94$ and 7.06, so $r = \boxed{11.5a_0/Z}$ and $\boxed{3.53a_0/Z}$. Substituting $Z = 1$ and $a_0 = 5.292 \times 10^{-11}$ m, $r = \boxed{607 \text{ pm}}$ and $\boxed{187 \text{ pm}}$.

The other maximum in the wavefunction is at $\boxed{r = 0}$. It is a physical maximum, but not a calculus maximum: the first derivative of the wavefunction does not vanish there, so it cannot be found by differentiation.

E9.7(b) The radial distribution function varies as

$$P = 4\pi r^2 \psi^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0} \text{ [9.17]}$$

The maximum value of P occurs at $r = a_0$ since

$$\frac{dP}{dr} \propto \left(2r - \frac{2r^2}{a_0}\right) e^{-2r/a_0} = 0 \quad \text{at} \quad r = a_0 \text{ and } P_{\max} = \frac{4}{a_0} e^{-2}$$

P falls to a fraction f of its maximum given by

$$f = \frac{\frac{4r^2}{a_0^3} e^{-2r/a_0}}{\frac{4}{a_0} e^{-2}} = \frac{r^2}{a_0^2} e^2 e^{-2r/a_0}$$

and hence we must solve for r in

$$\frac{f^{1/2}}{e} = \frac{r}{a_0} e^{-r/a_0}$$

(a) $f = 0.50$

$$0.260 = \frac{r}{a_0} e^{-r/a_0} \text{ solves to } r = 2.08a_0 = \boxed{110 \text{ pm}} \text{ and to } r = 0.380a_0 = \boxed{20.1 \text{ pm}}$$

(b) $f = 0.75$

$$0.319 = \frac{r}{a_0} e^{-r/a_0} \text{ solves to } r = 1.63a_0 = \boxed{86 \text{ pm}} \text{ and to } r = 0.555a_0 = \boxed{29.4 \text{ pm}}$$

In each case the equation is solved numerically (or graphically) with readily available personal computer software. The solutions above are easily checked by substitution into the equation for f. The radial distribution function is readily plotted and is shown in Figure 9.1.

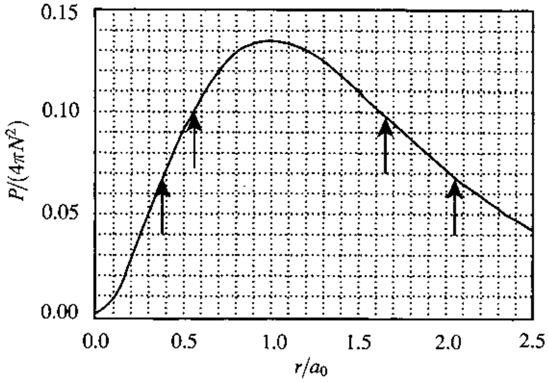


Figure 9.1

E9.8(b) The complete radial wavefunction, $R_{4,1}$ is not given in Table 9.1, but by consulting other references, such as *Introduction to Quantum Mechanics* by Pauling and Wilson, we learn that $R_{4,1}$ is proportional to

$$(20-10\rho+\rho^2)\rho, \quad \text{where} \quad \rho=\frac{2Zr}{na_0}$$

The radial nodes occur where the radial wavefunction vanishes, namely where

$$(20-10\rho+\rho^2)\rho=0.$$

The zeros of this function occur at

$$\rho=0, \quad \boxed{r=0}$$

and when

$$(20-10\rho+\rho^2)=0, \quad \text{with roots} \quad \rho=2.764, \quad \text{and} \quad \rho=7.236$$

then $r=\dfrac{4\rho a_0}{2Z}=\dfrac{4\rho a_0}{2}=\dfrac{11.056a_0}{2}=\boxed{5.528a_0}$ and $\dfrac{28.944a_0}{2}=\boxed{14.472a_0}$

or $r=\boxed{2.92\times10^{-10}\,\text{m}}$ and $\boxed{7.66\times10^{-10}\,\text{m}}$

E9.9(b) The average kinetic energy is

$$\langle\hat{E}_K\rangle=\int\psi^*\hat{E}_K\psi\,\mathrm{d}\tau$$

where $\psi=N(2-\rho)e^{-\rho/2}$ with $N=\dfrac{1}{4}\left(\dfrac{Z^3}{2\pi a_0^3}\right)^{1/2}$.

(**Note:** ρ is defined here as in Table 9.1.)

$$\hat{E}_K=-\frac{\hbar^2}{2m}\nabla^2 \quad \mathrm{d}\tau=r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi=\frac{a_0^3\rho^2\sin\theta\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi}{Z^3}$$

In spherical polar coordinates, three of the derivatives in ∇^2 are derivatives with respect to angles, so those parts of $\nabla^2\psi$ vanish. Thus,

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} = \frac{\partial^2\psi}{\partial\rho^2}\left(\frac{\partial\rho}{\partial r^2}\right)^2 + \frac{2Z}{\rho a_0}\left(\frac{\partial\psi}{\partial\rho}\right)\frac{\partial\rho}{\partial r} = \left(\frac{Z}{a_0}\right)^2 \times \left(\frac{\partial^2\psi}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial\psi}{\partial\rho}\right)$$

$$\frac{\partial\psi}{\partial\rho} = N(2-\rho)\times(-\tfrac{1}{2})\mathrm{e}^{-\rho/2} - N\ \mathrm{e}^{-\rho/2} = N(\tfrac{1}{2}\rho - 2)\mathrm{e}^{-\rho/2}$$

$$\frac{\partial^2\psi}{\partial\rho^2} = N(\tfrac{1}{2}\rho - 2)\times(-\tfrac{1}{2})\mathrm{e}^{-\rho/2} + \tfrac{1}{2}N\,\mathrm{e}^{-\rho/2} = N(\tfrac{3}{2} - \tfrac{1}{4}\rho)\mathrm{e}^{-\rho/2}$$

$$\nabla^2\psi = \left(\frac{Z}{a_0}\right)^2 N\mathrm{e}^{-\rho/2}(-4/\rho + 5/2 - \rho/4)$$

and

$$\langle\hat{E}_{\mathrm{K}}\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} N(2-\rho)\mathrm{e}^{-\rho/2}\left(\frac{Z}{a_0}\right)^2 \times \left(\frac{-\hbar^2}{2m}\right)$$
$$\times\ N\mathrm{e}^{-\rho/2}(-4/\rho + 5/2 - \rho/4)\frac{a_0^3\,\mathrm{d}\phi\sin\theta\,\mathrm{d}\theta\,\rho^2\,\mathrm{d}\rho}{Z^3}$$

The integrals over angles give a factor of 4π, so

$$\langle\hat{E}_{\mathrm{K}}\rangle = 4\pi N^2\left(\frac{a_0}{Z}\right)\times\left(-\frac{\hbar^2}{2m}\right)\int_0^\infty (2-\rho)\times(-4 + \tfrac{5}{2}\rho - \tfrac{1}{4}\rho^2)\rho\mathrm{e}^{-\rho}\,\mathrm{d}\rho$$

The integral in this last expression works out to -2, using $\int_0^\infty \mathrm{e}^{-\rho}\rho^n\,\mathrm{d}\rho = n!$ for $n = 1, 2,$ and 3, so

$$\langle\hat{E}_{\mathrm{K}}\rangle = 4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(\frac{a_0}{Z}\right)\times\left(\frac{\hbar^2}{m}\right) = \boxed{\frac{\hbar^2 Z^2}{8ma_0^2}}$$

The average potential energy is

$$\langle V\rangle = \int\psi^* V\psi\,\mathrm{d}\tau, \quad \text{where} \quad V = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{Z^2e^2}{4\pi\varepsilon_0 a_0\rho}$$

and $\langle V\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} N(2-\rho)\mathrm{e}^{-\rho/2}\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0\rho}\right)N(2-\rho)\mathrm{e}^{-\rho/2}\frac{a_0^3\rho^2\sin\theta\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi}{Z^3}$

The integrals over angles give a factor of 4π, so

$$\langle V\rangle = 4\pi N^2\left(-\frac{Z^2e^2}{4\pi\varepsilon_0\alpha_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\int_0^\infty (2-\rho)^2\rho\mathrm{e}^{-\rho}\,\mathrm{d}\rho$$

The integral in this last expression works out to 2, using $\int_0^\infty \mathrm{e}^{-\rho}\rho^n\mathrm{d}\rho = n!$ for $n = 1, 2, 3,$ and 4, so

$$\langle V\rangle = 4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\times(2) = \boxed{-\frac{Z^2e^2}{16\pi\varepsilon_0 a_0}}$$

E9.10(b) The radial distribution function is defined as

$$P = 4\pi r^2\psi^2 \quad \text{so} \quad P_{3s} = 4\pi r^2(Y_{0,0}R_{3,0})^2$$

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

where $\rho \int \dfrac{2Zr}{na_0} = \dfrac{2Zr}{3a_0}$ here.

We want to find the most likely radius, so it would help to simplify the function by expressing it in terms either of r or ρ, but not both. To find the most likely radius, we could set the derivative of P_{3s} equal to zero, therefore we can collect all multiplicative constants together (including the factors of a_0/Z needed to turn the initial r^2 into ρ^2) since they will eventually be divided into zero:

$$P_{3s} = C^2\rho^2(6-6\rho+\rho^2)^2\mathrm{e}^{-\rho}$$

Note that not all the extrema of P are maxima, some are minima, but all the extrema of $(P_{3s})^{1/2}$ correspond to maxima of P_{3s}, so let us find the extrema of $(P_{3s})^{1/2}$:

$$\frac{\mathrm{d}(P_{3s})^{1/2}}{\mathrm{d}\rho} = 0 = \frac{\mathrm{d}}{\mathrm{d}\rho}C\rho(6-6\rho+\rho^2)\mathrm{e}^{-\rho/2}$$

$$= C[\rho(6-6\rho+\rho^2)\times(-\tfrac{1}{2})+(6-12\rho+3\rho^2)]\mathrm{e}^{-\rho/2}$$

$$0 = C(6-15\rho+6\rho^2-\tfrac{1}{2}\rho^3)\mathrm{e}^{-\rho/2} \quad \text{so} \quad 12-30\rho+12\rho^2-\rho^3=0$$

Numerical solution of this cubic equation yields

$$\rho = 0.49, 2.79, \text{and } 8.72$$

corresponding to

$$r = \boxed{0.74a_0/Z,\ 4.19a_0/Z,\ \text{and } 13.08a_0/Z}$$

COMMENT. If numerical methods are to be used to locate the roots of the equation that locates the extrema, then graphical/numerical methods might as well be used to locate the maxima directly, that is, the student may simply have a spreadsheet compute P_{3s} and examine or manipulate the spreadsheet to locate the maxima.

E9.11(b) The radial distribution function is defined as

$$P = r^2R(r)^2 \quad \text{so} \quad P_{3p} = r^2(R_{3,1})^2,$$

$$\boxed{P_{3p} = C^2\times\rho^2(4-\rho)^2\rho^2\mathrm{e}^{-\rho}}$$

where $\rho \equiv \dfrac{2Zr}{na_0} = \dfrac{2Zr}{3a_0}$ here.

We want to find the most likely radius, so it would help to simplify the function by expressing it in terms either of r or ρ but not both. To find the most likely radius, we could set the derivative of P_{3p} equal to zero, therefore we can collect all multiplicative constants together (including the factors of a_0/Z needed to turn the initial r^2 into ρ^2) since they will eventually be divided into zero.

Note that not all the extrema of P are maxima, some are minima, but all the extrema of $(P_{3p})^{1/2}$ correspond to maxima of P_{3p}, so let us find the extrema of $(P_{3p})^{1/2}$:

$$\frac{d(P_{3p})^{1/2}}{d\rho} = 0 = \frac{d}{d\rho}C\rho^2(4-\rho)e^{-\rho/2}$$

$$= C[\rho(8-5\rho+\rho^2/2)]e^{-\rho/2}$$

so $8 - 5\rho + \rho^2/2 = 0$

The numerical solution of this quadratic equation yields

$\rho = 2$, and 8

corresponding to

$r = 3a_0/Z$ and $12a_0/Z$

$P(r)$ is larger at $12a_0$ than at $3a_0$, so the most probable position is $\boxed{r = 12a_0/Z.}$

COMMENT. If numerical methods are to be used to locate the roots of the equation that locates the extrema, then graphical/numerical methods might as well be used to locate the maxima directly, that is, the student may simply have a spreadsheet compute P_{3p} and examine or manipulate the spreadsheet to locate the maxima.

E9.12(b) Orbital angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = \hbar(l(l+1))^{1/2}$$

There are l angular nodes and $n - l - 1$ radial nodes.

(a) $n = 4$, $l = 2$, so $\langle \hat{L}^2 \rangle^{1/2} = 6^{1/2}\hbar = \boxed{2.45 \times 10^{-34}\ \text{J s}}$ $\boxed{2}$ angular nodes $\boxed{1}$ radial node

(b) $n = 2$, $l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\ \text{J s}}$ $\boxed{1}$ angular nodes $\boxed{0}$ radial nodes

(c) $n = 3$, $l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\ \text{J s}}$ $\boxed{1}$ angular node $\boxed{1}$ radial node

E9.13(b) See Figures 8.35 and 9.16 as well as Table 8.2 of the text. The number of angular nodes is the value of the quantum number l, which for d orbitals is 2. Hence, each of the five d-orbitals has two angular nodes. To locate the angular nodes look for the values of θ that make the wavefunction zero.

d_{z^2} orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The nodal planes are difficult to picture. $\boxed{\theta = 0.95532}$ is the angular node for both planes.

d_{xy} orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the $\boxed{xz \text{ and } yz \text{ planes}}$, and $\boxed{\theta = 0}$ is the angular node for both planes.

d_{yz} orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the $\boxed{xz \text{ and } xy \text{ planes}}$, and $\boxed{\theta = 0 \text{ and } \pi/2}$, respectively, are the angular nodes of these planes.

d_{xz} orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the $\boxed{yz \text{ and } xy \text{ planes}}$, and $\boxed{\theta = 0 \text{ and } \pi/2}$, respectively, are the angular nodes of these planes.

$d_{x^2-y^2}$ orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal $\boxed{\text{planes at } \phi = \pi/4 \text{ and } \phi = 3\pi/4}$, respectively, and $\boxed{\theta = 0}$ is the angular node of both of these planes.

E9.14(b) (a) 5d → 2s is $\boxed{\text{not}}$ an allowed transition, for $\Delta l = -2$ (Δl must equal ±1).

(b) 5p → 3s is $\boxed{\text{allowed}}$, since $\Delta l = -1$.

(c) 5p → 3f is $\boxed{\text{not}}$ allowed, for $\Delta l = +2$ (Δl must equal ±1).

E9.15(b) A source approaching an observer appears to be emitting light of frequency:

$$\nu_{\text{approaching}} = \frac{\nu}{1-\frac{s}{c}} \; [9.37\text{b}]$$

Since $\nu \propto \dfrac{1}{\lambda}$, $\lambda_{\text{obs}} = \left(1-\dfrac{s}{c}\right)\lambda$

For the light to appear green the speed would have to be

$$s = \left(1-\frac{\lambda_{\text{obs}}}{\lambda}\right)c = (2.998\times10^{8}\ \text{m s}^{-1})\times\left(1-\frac{530\ \text{nm}}{680\ \text{nm}}\right) = \boxed{6.61\times10^{7}\ \text{m s}^{-1}}$$

or about 1.4×10^{8} mph.

(Since $s \approx c$, the relativistic expression

$$\nu_{\text{obs}} = \left(\frac{1+\frac{s}{c}}{1-\frac{s}{c}}\right)^{1/2}\nu$$

should really be used. It gives $s = 6.02\times10^{7}\ \text{m s}^{-1}$.

E9.16(b) The linewidth is related to the lifetime τ by

$$\delta\tilde{\nu} = \frac{5.31\ \text{cm}^{-1}}{\tau/\text{ps}} \text{ [equation in \textit{Brief Illustration} in Section 9.6(b)] so } \tau = \frac{5.31\ \text{cm}^{-1}}{\delta\tilde{\nu}}\,\text{ps}$$

(a) We are given a frequency rather than a wavenumber

$$\tilde{\nu} = \nu/c, \quad \text{so} \quad \tau = \frac{(5.31\ \text{cm}^{-1})\times(2.998\times10^{10}\ \text{cm s}^{-1})}{200\times10^{6}\ \text{s}^{-1}}\,\text{ps} = \boxed{7.96\times10^{2}\ \text{ps}}$$

(b) $\tau = \dfrac{5.31\ \text{cm}^{-1}}{2.45\ \text{cm}^{-1}}\,\text{ps} = \boxed{2.14\ \text{ps}}$

E9.17(b) The linewidth is related to the lifetime τ by

$$\delta\tilde{\nu} = \frac{5.31\ \text{cm}^{-1}}{\tau/\text{ps}} \text{ [equation in \textit{Brief illustration}], so } \delta\nu = \frac{(5.31\ \text{cm}^{-1})c}{\tau/\text{ps}}$$

(a) If every collision is effective, then the lifetime is $1/(1.0\times10^{9}\ \text{s}^{-1}) = 1.0\times10^{-9}\ \text{s} = 1.0\times10^{3}\ \text{ps}$

$$\delta\nu = \frac{(5.31\ \text{cm}^{-1})\times(2.998\times10^{10}\ \text{cm s}^{-1})}{1.0\times10^{3}} = 1.6\times10^{8}\ \text{s}^{-1} = \boxed{160\ \text{MHz}}$$

(b) If only one collision in 10 is effective, then the lifetime is a factor of 10 greater, 1.0×10^4 ps

$$\delta\nu = \frac{(5.31\ \mathrm{cm^{-1}}) \times (2.998 \times 10^{10}\ \mathrm{cm\ s^{-1}})}{1.0 \times 10^4} = 1.6 \times 10^7\ \mathrm{s^{-1}} = \boxed{16\ \mathrm{MHz}}$$

E9.18(b) Y: $[\mathrm{Kr}]5\mathrm{s}^2 4\mathrm{d}^1$

Zr: $[\mathrm{Kr}]5\mathrm{s}^2 4\mathrm{d}^2$

Nb: $[\mathrm{Kr}]5\mathrm{s}^2 4\mathrm{d}^3$ or $[\mathrm{Kr}]5\mathrm{s}^1 4\mathrm{d}^4$ (most probable)

Mo: $[\mathrm{Kr}]5\mathrm{s}^1 4\mathrm{d}^5$

Tc: $[\mathrm{Kr}]5\mathrm{s}^2 4\mathrm{d}^5$

Ru: $[\mathrm{Kr}]5\mathrm{s}^2 4\mathrm{d}^6$ or $[\mathrm{Kr}]5\mathrm{s}^1 4\mathrm{d}^7$ (most probable)

Rh: $[\mathrm{Kr}]5\mathrm{s}^1 4\mathrm{d}^8$

Pd: $[\mathrm{Kr}]5\mathrm{s}^1 4\mathrm{d}^9$ or $[\mathrm{Kr}]4\mathrm{d}^{10}$ (most probable)

Ag: $[\mathrm{Kr}]5\mathrm{s}^1 4\mathrm{d}^{10}$

Cd: $[\mathrm{Kr}]5\mathrm{s}^2 4\mathrm{d}^{10}$

E9.19(b) $\mathrm{V}^{2+}: 1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^6 3\mathrm{s}^2 3\mathrm{p}^6 3\mathrm{d}^3 = [\mathrm{Ar}]3\mathrm{d}^3$

The only unpaired electrons are those in the 3d subshell. There are three, $S = \boxed{\frac{3}{2}}$ and $\frac{3}{2} - 1 = \boxed{\frac{1}{2}}$.

For $S = \frac{3}{2}$, $M_S = \boxed{\pm\frac{1}{2} \text{ and } \pm\frac{3}{2}}$

For $S = \frac{1}{2}$, $M_S = \boxed{\pm\frac{1}{2}}$

E9.20(b) For $l > 0, j = l \pm 1/2$, so

(a) $l = 1$, so $j = \boxed{1/2 \text{ of } 3/2}$

(b) $l = 5$, so $j = \boxed{9/2 \text{ or } 11/2}$

E9.21(b) Use the Clebsch–Gordan series in the form

$$J = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|$$

Then, with $j_1 = 5$ and $j_2 = 3$

$$J = \boxed{8, 7, 6, 5, 4, 3, 2}$$

E9.22(b) 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.

E9.23(b) (a) Possible values of S for four electrons in different orbitals are $\boxed{2, 1, \text{ and } 0}$; the multiplicity is $2S + 1$, so multiplicities are $\boxed{5, 3, \text{ and } 1}$, respectively.

(b) Possible values of S for five electrons in different orbitals are $\boxed{5/2,\ 3/2 \text{ and } 1/2}$; the multiplicity is $2S+1$, so multiplicities are $\boxed{6,\ 4, \text{ and } 2}$, respectively.

E9.24(b) The coupling of a p electron ($l=1$) and a d electron ($l=2$) gives rise to $L=3$ (F), 2 (D), and 1 (P) terms. Possible values of S include 0 and 1. Possible values of J (using Russell–Saunders coupling) are 3, 2, and 1 ($S=0$) and 4, 3, 2, 1, and 0 ($S=1$). The term symbols are

$$\boxed{{}^1F_3;\ {}^3F_4,\ {}^3F_3,\ {}^3F_2;\ {}^1D_2;\ {}^3D_3,\ {}^3D_2,\ {}^3D_1;\ {}^1P_1,\ {}^3P_2,\ {}^3P_1,\ {}^3P_0}$$

Hund's rules state that the lowest energy level has maximum multiplicity. Consideration of spin–orbit coupling says the lowest energy level has the lowest value of $J(J+1)-L(L+1)-S(S+1)$. So, the lowest energy level is $\boxed{{}^3F_2}$.

E9.25(b) (a) ^{3}D has $S=1$ and $L=2$, so $J=\boxed{3,\ 2, \text{ and } 1}$ are present. $J=3$ has $\boxed{7}$ states, with $M_J=0, \pm1, \pm2$, or ±3; $J=2$ has $\boxed{5}$ states, with $M_J=0, \pm1$, or ±2; $J=1$ has $\boxed{3}$ states, with $M_J=0$, or ±1.

(b) ^{4}D has $S=3/2$ and $L=2$, so $J=\boxed{7/2,\ 5/2,\ 3/2 \text{ and } 1/2}$, are present. $J=7/2$ has $\boxed{8}$ possible states, with $M_J=\pm7/2, \pm5/2, \pm3/2$ or $\pm1/2$; $J=5/2$ has $\boxed{6}$ possible states, with $M_J=\pm5/2\ \pm3/2$ or $\pm1/2$; $J=3/2$ has $\boxed{4}$ possible states, with $M_J=\pm3/2$ or $\pm1/2$; $J=1/2$ has $\boxed{2}$ possible states, with $M_J=\pm1/2$.

(c) ^{2}G has $S=1/2$ and $L=4$, so $J=9/2$ and $7/2$ are present. $J=9/2$ had $\boxed{10}$ possible states, with $M_J=\pm9/2, \pm7/2, \pm5/2, \pm3/2$ or $\pm1/2$, $J=7/2$ has $\boxed{8}$ possible states, with $M_J=\pm7/2, \pm5/2, \pm3/2$ or $\pm1/2$.

E9.26(b) Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

(a) Sc[Ar]$3d^14s^2$: $S=\frac{1}{2}$, $L=2$; $J=\frac{5}{2}, \frac{3}{2}$, so the terms are $\boxed{{}^2D_{5/2} \text{ and } {}^2D_{3/2}}$.

(b) Br[Ar]$3d^{10}4s^24p^5$. We treat the missing electron in the $4p$ subshell as equivalent to a single 'electron' with $l=1$, $S=\frac{1}{2}$. Hence, $L=1$, $S=\frac{1}{2}$, and $J=\frac{3}{2}, \frac{1}{2}$, so the terms are $\boxed{{}^2P_{3/2} \text{ and } {}^2P_{1/2}}$.

E9.27(b) See eqn 9.46 for the selection rules. (a) $\boxed{\text{allowed}}$, (b) $\boxed{\text{allowed}}$, (c) $\boxed{\text{forbidden}}$.

Solutions to problems

Solutions to numerical problems

P9.2 All lines in the hydrogen spectrum fit the Rydberg formula:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\left[9.1, \text{ with } \tilde{\nu} = \frac{1}{\lambda}\right] \quad R_H = 109\,677\ \text{cm}^{-1}$$

Find n_1 from the value of $\lambda_{\max}$, which arises from the transition $n_1+1 \rightarrow n_1$ $\dfrac{1}{\lambda_{\max}R_H} = \dfrac{1}{n_1^2} - \dfrac{1}{(n_1+1)^2}$

$$= \frac{2n_1+1}{n_1^2(n_1+1)^2}$$

$$\lambda_{\max}R_{\mathrm{H}} = \frac{n_1^2(n_1+1)^2}{2n_1+1} = (656.46\times10^{-9}\,\mathrm{m})\times(109\,677\times10^{2}\,\mathrm{m}^{-1}) = 7.20$$

and hence $n_1 = 2$, as determined by trial and error substitution. Therefore, the transitions are given by

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4}-\frac{1}{n_2^2}\right),\quad n_2 = 3, 4, 5, 6$$

The next line has $n_2 = 7$, and occurs at

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4}-\frac{1}{49}\right) = \boxed{397.13\,\mathrm{nm}}$$

The energy required to ionize the atom is obtained by letting $n_2 \to \infty$. Then,

$$\tilde{\nu}_\infty = \frac{1}{\lambda_\infty} = (109\,677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4}-0\right) = 27\,419\,\mathrm{cm}^{-1},\quad \text{or}\quad \boxed{3.40\,\mathrm{eV}}$$

(The answer, 3.40 eV, is the ionization energy of an H atom that is already in an excited state, with $n = 2$.)

COMMENT. The series with $n_1 = 2$ is the Balmer series.

P9.4 The lowest possible value of n in $1s^2nd^1$ is 3, thus the series of ^2D terms correspond to $1s^23d$, $1s^24d$, etc. Figure 9.2 is a description consistent with the data in the problem statement.

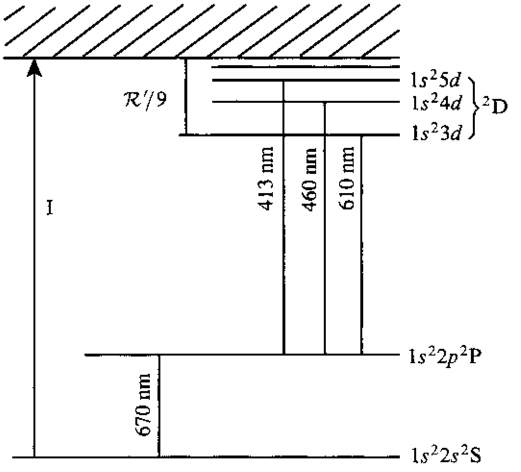


Figure 9.2

If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, {}^2D) = -\frac{hcR'}{n^2}\quad [n = 3, 4, 5, \ldots]$$

Then, for the $^2D \to {}^2P$ transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^22p^1, {}^2P)|}{hc} - \frac{R'}{n^2}\quad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu},\ \tilde{\nu} = \frac{\Delta E}{hc}\right]$$

from which we can write

$$\frac{|E(1s^2 2p^1, {}^2P)|}{hc} = \frac{1}{\lambda} + \frac{R'}{n^2} = \begin{cases} \dfrac{1}{610.36 \times 10^{-7}\,\text{cm}} + \dfrac{R'}{9} & \text{(a)} \\[2ex] \dfrac{1}{460.29 \times 10^{-7}\,\text{cm}} + \dfrac{R'}{16} & \text{(b)} \\[2ex] \dfrac{1}{413.23 \times 10^{-7}\,\text{cm}} + \dfrac{R'}{25} & \text{(c)} \end{cases}$$

$$\text{Then, } \left.\begin{array}{l} \text{(b)} - \text{(a) solves to } R' = 109\,886\ \text{cm}^{-1} \\ \text{(a)} - \text{(c) solves to } R' = 109\,910\ \text{cm}^{-1} \\ \text{(b)} - \text{(c) solves to } R' = 109\,963\ \text{cm}^{-1} \end{array}\right\} \text{Mean} = 109\,920\ \text{cm}^{-1}$$

The binding energies are therefore

$$E(1s^2 3d^1, {}^2D) = -\frac{R'}{9} = -12\,213\ \text{cm}^{-1}$$

$$E(1s^2 2p^1, {}^2P) = -\frac{1}{610.36 \times 10^{-7}\,\text{cm}} - 12\,213\ \text{cm}^{-1} = -28\,597\ \text{cm}^{-1}$$

$$E(1s^2 2s^1, {}^2S) = -\frac{1}{670.78 \times 10^{-7}\,\text{cm}} - 28\,597\ \text{cm}^{-1} = -43\,505\ \text{cm}^{-1}$$

Therefore, the ionization energy is

$$I(1s^2 2s^1, {}^2S) = 43\,505\ \text{cm}^{-1}, \quad \text{or} \quad \boxed{5.39\ \text{eV}}$$

P9.6 The ground term is $[\text{Ar}]4s^1\ {}^2S_{1/2}$ and the first excited term is $[\text{Ar}]4p^1\ {}^2P$. The latter has two levels, with $J = 1 + \frac{1}{2} = \frac{3}{2}$ and $J = 1 - \frac{1}{2} = \frac{1}{2}$, which are split by spin–orbit coupling (Section 9.9), therefore ascribe the transitions to $\boxed{{}^2P_{3/2} \to {}^2S_{1/2}}$ and $\boxed{{}^2P_{1/2} \to {}^2S_{1/2}}$ (since both are allowed). For these values of J, the splitting is equal to $\frac{3}{2}A$ (Example 9.5). Hence, since

$$(766.70 \times 10^{-7}\ \text{cm})^{-1} - (770.11 \times 10^{-7}\ \text{cm})^{-1} = 57.75\ \text{cm}^{-1}$$

we can conclude that $A = \boxed{38.50\,\text{cm}^{-1}}$.

P9.8 The Rydberg constant for positronium (R_{Ps}) is given by

$$R_{\text{Ps}} = \frac{R_\infty}{1 + \frac{m_e}{m_e}} = \frac{R_\infty}{1+1} = \frac{1}{2}R_\infty \quad [9.15;\ \text{also Problem 9.7};\ m(\text{positron}) = m_e]$$

$$= 54\,869\ \text{cm}^{-1} \quad [R = 109\,737\ \text{cm}^{-1}]$$

Hence,

$$\tilde{\nu} = \frac{1}{\lambda} = (54\,869\ \text{cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n^2}\right), \quad n = 3, 4, \ldots$$

$$= \boxed{7621\ \text{cm}^{-1}}, \boxed{10\,288\ \text{cm}^{-1}}, \boxed{11\,522\ \text{cm}^{-1}}, \ldots$$

The binding energy of Ps is

$$E = -hcR_{\text{Ps}}, \text{ corresponding to } (-)54\,869\text{ cm}^{-1}$$

The ionization energy is therefore 54 869 cm^{-1}, or $\boxed{6.80\text{ eV}}$.

P9.10 If we assume that the innermost electron is a hydrogen-like 1s orbital we may write

$$r^* = \frac{a_0}{Z}\,[\text{Example 9.3}] = \frac{52.92\text{ pm}}{126} = \boxed{0.420\text{ pm}}$$

P9.12 On the assumption that every collision deactivates the molecule, we may write

$$\tau = \frac{1}{z} = \boxed{\frac{kT}{4\sigma p}\left(\frac{\pi m}{kT}\right)^{1/2}}$$

For HCl, with $m \approx 36$ u,

$$\tau \approx \left(\frac{(1.381\times10^{-23}\text{ J K}^{-1})\times(298\text{ K})}{(4)\times(0.30\times10^{-18}\text{ m}^2)\times(1.013\times10^5\text{ Pa})}\right)\times\left(\frac{\pi\times(36)\times(1.661\times10^{-27}\text{ kg})}{(1.381\times10^{-23}\text{ J K}^{-1})\times(298\text{ K})}\right)^{1/2}$$

$$\approx 2.3\times10^{-10}\text{ s}$$

$$\delta E \approx h\delta\nu = \frac{\hbar}{\tau}\ [9.39]$$

The width of the collision-broadened line is therefore approximately

$$\delta\nu \approx \frac{1}{2\pi\tau} = \frac{1}{(2\pi)\times(2.3\times10^{-10}\text{ s})} \approx \boxed{700\text{ MHz}}$$

The Doppler width is approximately 1.3 MHz (see the following calculation).

To calculate the Doppler width we need the relationship

$$\frac{\delta\lambda}{\lambda} = \frac{2}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2}\ [9.38]$$

$$= \left(\frac{2}{2.998\times10^8\text{ m s}^{-1}}\right)\times\left(\frac{(2)\times(1.381\times10^{-23}\text{ J K}^{-1})\times(298\text{ K})\times(\ln 2)}{(m/\text{u})\times(1.6605\times10^{-27}\text{ kg})}\right)^{1/2} = \frac{1.237\times10^{-5}}{(m/\text{u})^{1/2}}$$

For $^1\text{H}^{35}\text{Cl}$, $m \approx 36$ u, so $\dfrac{\delta\lambda}{\lambda} \approx \boxed{2.1\times10^{-6}}$

For HCl, $\nu(\text{rotation}) \approx 2\tilde{B}c \approx (2)\times(10.6\text{ cm}^{-1})\times(2.998\times10^{10}\text{ cm s}^{-1})$
$\approx 6.4\times10^{11}\text{s}^{-1}$ or 6.4×10^{11} Hz

Therefore, $\delta\nu(\text{rotation}) \approx (2.1\times10^{-6})\times(6.4\times10^{11}\text{ Hz}) = \boxed{1.3\text{ MHz}}$

Since the collision width is proportional to p [$\delta\nu \propto 1/\tau$ and $\tau \propto 1/p$], the pressure must be reduced by a factor of about $\dfrac{1.3}{700} = 0.002$ before Doppler broadening begins to dominate collision broadening. Hence, the pressure must be reduced to below

$$(0.002)\times(760\text{ Torr}) = \boxed{1\text{ Torr}}$$

Solutions to theoretical problems

P9.14 In each case we need to show that

$$\int_{\text{all space}} \psi_1^* \psi_2 \, \mathrm{d}\tau = 0$$

(a) $$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \psi_{1s}\psi_{2s} r^2 \, \mathrm{d}r \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \overset{?}{=} 0$$

$$\left.\begin{aligned}\psi_{1s} &= R_{1,0}Y_{0,0}\\ \psi_{2s} &= R_{2,0}Y_{0,0}\end{aligned}\right\} Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2} \text{[Table 8.2]}$$

Since $Y_{0,0}$ is a constant, the integral over the radial functions determines the orthogonality of the functions.

$$\int_0^{\infty} R_{1,0}R_{2,0} r^2 \, \mathrm{d}r$$

$$R_{1,0} \propto \mathrm{e}^{-\rho/2} = \mathrm{e}^{-Zr/a_0} \quad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$R_{2,0} \propto (2 - \rho/2)\mathrm{e}^{-\rho/4} = \left(2 - \frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0} \quad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$\int_0^{\infty} R_{1,0}R_{2,0} r^2 \, \mathrm{d}r \propto \int_0^{\infty} \mathrm{e}^{-Zr/a_0}\left(2 - \frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0} r^2 \, \mathrm{d}r$$

$$= \int_0^{\infty} 2\mathrm{e}^{-(3/2)Zr/a_0} r^2 \, \mathrm{d}r - \int_0^{\infty} \frac{Z}{a_0}\mathrm{e}^{-(3/2)Zr/a_0} r^3 \, \mathrm{d}r$$

$$= \frac{2 \times 2!}{\left(\frac{3}{2}\frac{z}{a_0}\right)^3} - \left(\frac{Z}{a_0}\right) \times \frac{3!}{\left(\frac{3}{2}\frac{z}{a_0}\right)^4} = \boxed{0}$$

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 9.2(g), eqn 9.22

$$\mathrm{p}_x \propto x, \quad \mathrm{p}_y \propto y$$

Thus,

$$\int_{\text{all space}} \mathrm{p}_x \mathrm{p}_y \, \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \propto \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} xy \, \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

This is an integral of an odd function of x and y over the entire range of variables from $-\infty$ to $+\infty$, therefore the $\boxed{\text{integral is zero}}$. More explicitly we may perform the integration using the orbitals in the form (Section 9.2(g), eqn 9.22):

$$p_x = f(r)\sin\theta\cos\phi \quad p_y = f(r)\sin\theta\sin\phi$$

$$\int_{\text{all space}} p_x p_y r^2\,dr\sin\theta\,d\theta\,d\phi = \int_0^{\infty} f(r)^2 r^2\,dr \int_0^{\pi}\sin^2\theta\,d\theta \int_0^{2\pi}\cos\phi\sin\phi\,d\phi$$

The first factor is non-zero since the radial functions are normalized. The second factor is $\frac{\pi}{2}$. The third factor is zero. Therefore, the product of the integrals is $\boxed{\text{zero}}$ and the functions are orthogonal.

P9.16 We use the p_x and p_y orbitals in the form (Section 9.2(g))

$$p_x = rf(r)\sin\theta\cos\phi \quad p_y = rf(r)\sin\theta\sin\phi$$

and use $\cos\phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi})$ and $\sin\phi = \frac{1}{2i}(e^{i\phi} - e^{-i\phi})$ then

$$p_x = \frac{1}{2}rf(r)\sin\theta\,(e^{i\phi} + e^{-i\phi}) \quad p_y = \frac{1}{2i}rf(r)\sin\theta\,(e^{i\phi} - e^{-i\phi})$$

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \text{ [Problem 8.28, Section 8.6, and eqn 8.46]}$$

$$\hat{l}_z p_x = \frac{\hbar}{2}rf(r)\sin\theta\,e^{i\phi} - \frac{\hbar}{2}rf(r)\sin\theta\,e^{-i\phi} = i\hbar p_y \neq \text{constant} \times p_x$$

$$\hat{l}_z p_y = \frac{\hbar}{2i^2}rf(r)\sin\theta\,e^{i\phi} + \frac{\hbar}{2i^2}rf(r)\sin\theta\,e^{-i\phi} = -i\hbar p_x \neq \text{constant} \times p_y$$

Therefore, neither p_x nor p_y are eigenfunctions of $\hat{l}_z$. However, $\boxed{p_x + ip_y \text{ and } p_x - ip_y}$ are eigenfunctions:

$$p_x + ip_y = rf(r)\sin\theta\,e^{i\phi} \quad p_x - ip_y = rf(r)\sin\theta\,e^{-i\phi}$$

since both $e^{i\phi}$ and $e^{-i\phi}$ are eigenfunctions of $\hat{l}_z$ with eigenvalues $+h$ and $-h$.

P9.18 $$\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}\,[9.17]$$

The probability of the electron being within a sphere of radius r' is

$$\int_0^{r'}\int_0^{\pi}\int_0^{2\pi} \psi_{1s}^2 r^2\,dr\,\sin\theta\,d\theta\,d\phi$$

We set this equal to 0.90 and solve for r'. The integral over θ and ϕ gives a factor of 4π, thus

$$0.90 = \frac{4}{a_0^3}\int_0^{r'} r^2 e^{-2r/a_0}\,dr$$

$\int_0^{r'} r^2 e^{-2r/a_0}dr$ is integrated by parts to yield $-\frac{a_0 r^2 e^{-2r/a_0}}{2}\Bigg|_0^{r'} + a_0\left[-\frac{a_0 r e^{-2r/a_0}}{2}\Bigg|_0^{r'} + \frac{a_0}{2}\left(-\frac{a_0 e^{-2r/a_0}}{2}\right)\Bigg|_0^{r'}\right]$

$$= -\frac{a_0(r')^2 e^{-2r'/a_0}}{2} - \frac{a_0^2 r'}{2}e^{-2r'/a_0} - \frac{a_0^3}{4}e^{-2r'/a_0} + \frac{a_0^3}{4}$$

Multiplying by $\frac{4}{a_0^3}$ and factoring e^{-2r'/a_0}

$$0.90 = \left[-2\left(\frac{r'}{a_0}\right)^2 - 2\left(\frac{r'}{a_0}\right) - 1\right]e^{-2r'/a_0} + 1 \text{ or } 2\left(\frac{r'}{a_0}\right)^2 + 2\left(\frac{r'}{a_0}\right) + 1$$
$$= 0.10e^{2r'/a_0}$$

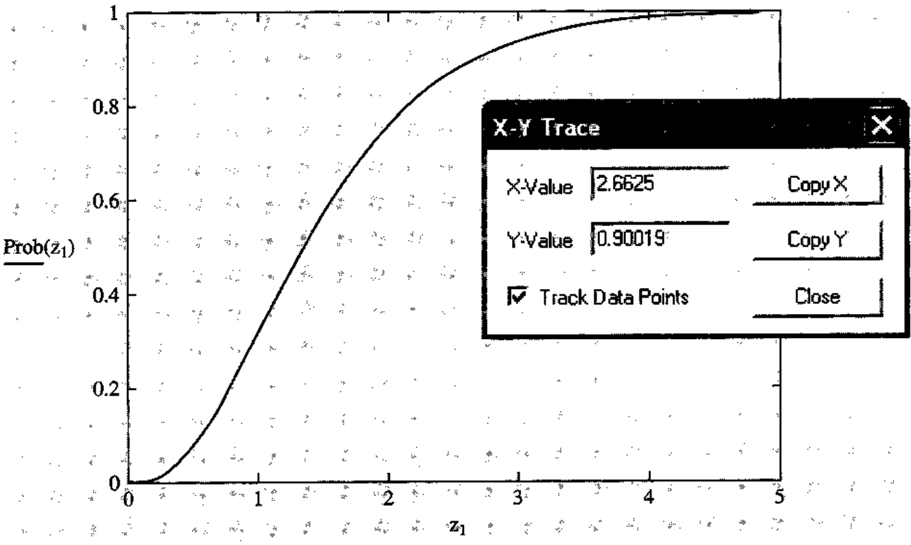
It is easiest to solve this numerically. It is seen that $\boxed{r' = 2.66\,a_0}$ satisfies the above equation.

Mathematical software has powerful features for handling this type of problem. Plots are very convenient to both make and use. Solve blocks can be used as functions. Both features are demonstrated below using Mathcad.

Let $z = r/a_0$. The probability, Prob(z), that a 1s electron is within a sphere of radius z is:

$$\text{Prob}(z) := 4 \cdot \int_0^z x^2 \cdot e^{-2 \cdot x}\,dx$$

Variables needed for plot: $N := 800$ $i := 0..N$ $z_{max} := 5$ $z_i := \frac{z_{max} \cdot i}{N}$



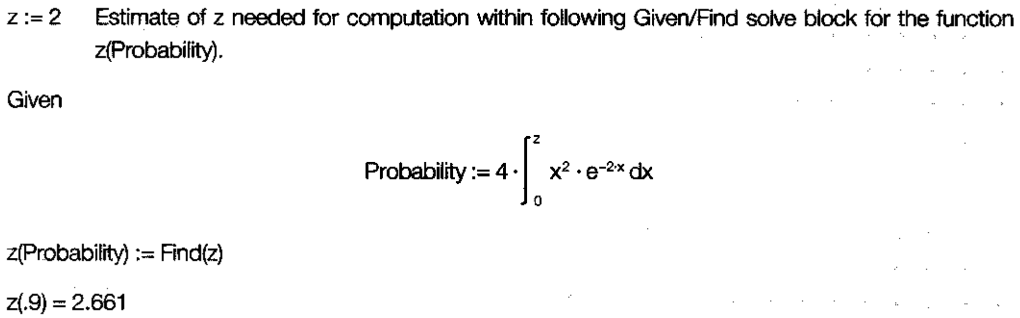
X-Value 2.6625

Y-Value 0.90019

☑ Track Data Points

The plot indicates that the probability of finding the electron in a sphere of radius z is sigmoidal. The trace feature of Mathcad is used to find that with $z = 2.66$ ($r = 2.66\,a_0$) there is a 90.0% probability of finding the electron in the sphere.

The following Mathcad document develops a function for calculating the radius for any desired probability. The probability is presented to the function as an argument



$z := 2$ Estimate of z needed for computation within following Given/Find solve block for the function z(Probability).

Given

$$\text{Probability} := 4 \cdot \int_0^z x^2 \cdot e^{-2 \cdot x}\,dx$$

z(Probability) := Find(z)

z(.9) = 2.661

P9.20 The attractive Coulomb force $= \dfrac{Ze^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{r^2}$

The repulsive centrifugal force $= \dfrac{(\text{angular momentum})^2}{m_e r^3} = \dfrac{(n\hbar)^2}{m_e r^3}$ [postulated]

The two forces balance when

$$\frac{Ze^2}{4\pi\varepsilon_0}\times\frac{1}{r^2} = \frac{n^2\hbar^2}{m_e r^3}, \quad \text{implying that} \quad r = \frac{4\pi n^2\hbar^2\varepsilon_0}{Ze^2 m_e}$$

The total energy is

$$E = E_K + V = \frac{(\text{angular momentum})^2}{2I} - \frac{Ze^2}{4\pi\varepsilon_0}\times\frac{1}{r} = \frac{n^2\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} \text{ [postulated]}$$

$$= \left(\frac{n^2\hbar^2}{2m_e}\right)\times\left(\frac{Ze^2 m_e}{4\pi n^2\hbar^2\varepsilon_0}\right)^2 - \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\times\left(\frac{Ze^2 m_e}{4\pi n^2\hbar^2\varepsilon_0}\right) = \boxed{-\frac{Z^2 e^4 m_e}{32\pi^2\varepsilon_0^2\hbar^2}\times\frac{1}{n^2}}$$

P9.22 Refer to Problems 9.8 and 9.20 and their solutions.

$$\mu_H = \frac{m_e m_p}{m_e + m_p} \approx m_e \quad [m_p = \text{mass of proton}]$$

$$\mu_{Ps} = \frac{m_e m_{pos}}{m_e + m_{pos}} = \frac{m_e}{2} \quad [m_{pos} = \text{mass of proton} = m_e]$$

$$a_0 = r(n = 1) = \frac{4\pi\hbar^2\varepsilon_0}{e^2 m_e} \text{ [9.11 and Problem 9.20]}$$

To obtain a_{Ps} the radius of the first Bohr orbit of positronium, we replace m_e with $\mu_{Ps} = \dfrac{m_e}{2}$, hence

$$\boxed{a_{Ps} = 2a_0} = \frac{\pi\hbar^2\varepsilon_0}{e^2 m_e}$$

The energy of the first Bohr orbit of positronium is

$$E_{1,\mathrm{Ps}} = -hcR_{\mathrm{Ps}} = -\frac{hc}{2}R_{\infty} \text{ [Problem 9.8]}$$

Thus, $\boxed{E_{1,\mathrm{Ps}} = \frac{1}{2}E_{1,\mathrm{H}}}$

Question. What modifications are required in these relationships when the finite mass of the hydrogen nucleus is recognized?

P9.24 (a) The speed distribution in the molecular beam is related to the speed distribution within the chamber by a factor of $v\cos\theta$, as shown in Figure 9.3. Since an integration over all possible θ must be performed, the $\cos\theta$ factor may be absorbed into the constant of proportionality:

$$f_{\mathrm{beam}}(v) = Cvf_{\mathrm{chamber}}(v), \quad \text{where } C \text{ is to be determined}$$

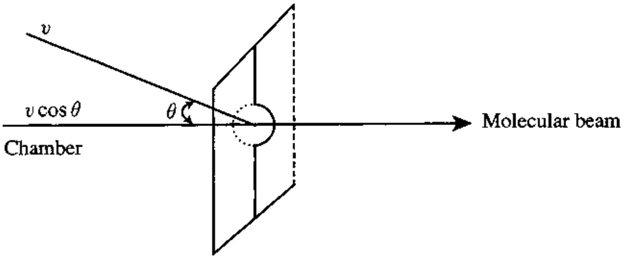


Figure 9.3

By normalization over the possible beam speeds ($0 < v_{\mathrm{beam}} < \infty$)

$$f_{\mathrm{beam}} = Cv(v^2 e^{-(mv^2/2kT)}) = Cv^3 e^{-(mv^2/2kT)}$$

$$\int_{v=0}^{\infty} f_{\mathrm{beam}}\,\mathrm{d}v = 1 = C\int_{v=0}^{\infty} v^3 e^{-(mv^2/2kT)}\,\mathrm{d}v = C\left\{\frac{1}{2(m/2kT)^2}\right\}$$

$$C = 2(m/2kT)^2$$

$$\langle v^2\rangle = \int_{v=0}^{\infty} v^2 f_{\mathrm{beam}}(v)\,\mathrm{d}v = C\int v^5 e^{-(mv^2/2kT)}\,\mathrm{d}v = C\left\{\frac{1}{(m/2kT)^3}\right\} = 2\frac{(m/2kT)^2}{(m/2kT)^3} = \frac{4kT}{m}$$

$$\langle E_{\mathrm{K}}\rangle = \frac{m}{2}\langle v^2\rangle = \frac{m}{2}\left(\frac{4kT}{m}\right) = \boxed{2kT}$$

(b) $$\Delta x = \left(\frac{2\mu_{\mathrm{B}}L^2}{4E_{\mathrm{K}}}\right)\frac{\mathrm{d}\mathcal{B}}{\mathrm{d}z}$$

or $$\frac{\mathrm{d}\mathcal{B}}{\mathrm{d}z} = \frac{4E_{\mathrm{K}}\Delta x}{2\mu_{\mathrm{B}}L^2} = \frac{4(2kT)\Delta x}{2\mu_{\mathrm{B}}L^2} = \frac{4kT\Delta x}{\mu_{\mathrm{B}}L^2} = \frac{4(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})\times(1000\,\mathrm{K})\times(1.00\times10^{-3}\,\mathrm{m})}{(9.27402\times10^{-24}\,\mathrm{J\,T^{-1}})\times(50\times10^{-2}\,\mathrm{m})^2}$$

$$\frac{\mathrm{d}\mathcal{B}}{\mathrm{d}z} = \boxed{23.8\,\mathrm{T\,m^{-1}}}$$

Solutions to applications

P9.26 A stellar surface temperature of 3000–4000K (a 'red star') doesn't have the energetic particles and photons that are required for either the collisional or radiative excitation of a neutral hydrogen atom. Atomic hydrogen affects neither the absorption nor the emission lines of red stars in the absence of excitation. 'Blue stars' have surface temperature of 15 000–20 000K. Both the kinetic energy and the black-body emissions display energies great enough to completely ionize hydrogen. Lacking an electron, the remaining proton cannot affect absorption and emission lines either.

In contrast, a star with a surface temperature of 8000–10 000K has a temperature low enough to avoid complete hydrogen ionization but high enough for black-body radiation to cause electronic transitions of atomic hydrogen. Hydrogen spectral lines are intense for these stars.

Simple kinetic energy and radiation calculations confirm these assertions. For example, a plot of black-body radiation against *hν/I*, where *I* is the ionization eneregy, is shown below (Figure 9.4).

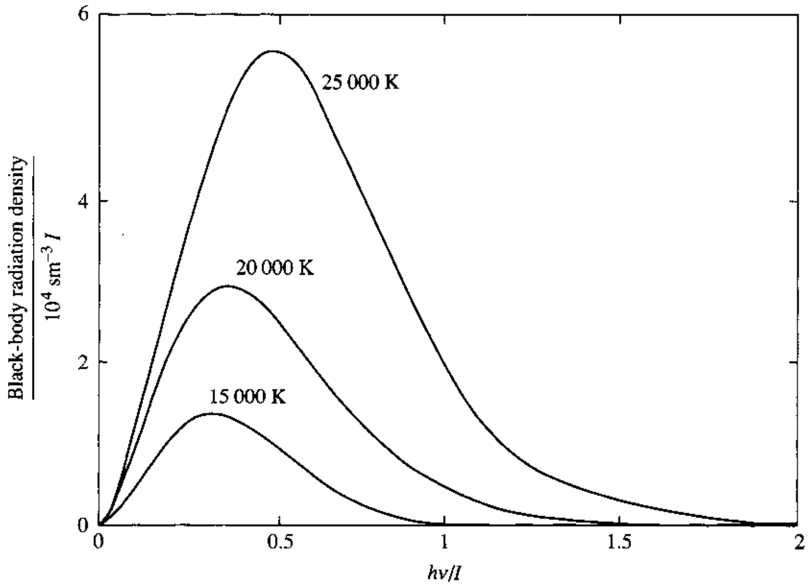


Figure 9.4

It is clearly seen that at 25 000K a large fraction of the radiation is able to ionize the hydrogen (*hν/I*). It is likely that at such high surface temperatures all hydrogen is ionized and, consequently, unable to affect spectra.

Alternatively, consider the equilibrium between hydrogen atoms and their component charged particles:

$$\mathrm{H} = \mathrm{H}^{+} + \mathrm{e}^{-}$$

The equilibrium constant is:

$$K = \frac{p_{+}p_{-}}{p_{\mathrm{H}}p^{\ominus}} = \exp\left(\frac{-\Delta G^{\ominus}}{RT}\right) = \exp\left(\frac{-\Delta H^{\ominus}}{RT}\right) \times \exp\left(\frac{\Delta S^{\ominus}}{R}\right).$$

P9.30 According to Problem 9.29, the Doppler effect obeys

$$\nu_{\text{receding}} = \nu f, \text{ where } f = \left(\frac{1 - s/c}{1 + s/c}\right)^{1/2}$$

This can be rearranged to yield:

$$s = \frac{1 - f^2}{1 + f^2}c$$

We are given wavelength data, so we use:

$$f = \frac{\nu_{\text{star}}}{\nu} = \frac{\lambda}{\lambda_{\text{star}}}$$

The ratio is:

$$f = \frac{654.2 \text{ nm}}{706.5 \text{ nm}} = 0.9260$$

$$\text{so} \quad s = \frac{1 - 0.9260^2}{1 + 0.9260^2}c = \boxed{0.0768c} = 2.30 \times 10^7 \text{ m s}^{-1}$$

The broadening of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the star. Eqn 9.38 relates the observed linewidth to temperature:

$$\delta\lambda_{\text{obs}} = \frac{2\lambda}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2}, \quad \text{so} \quad T = \left(\frac{c\delta\lambda}{2\lambda}\right)^2 \frac{m}{2k\ln 2}$$

$$T = \left(\frac{(2.998 \times 10^8 \text{ m s}^{-1})(61.8 \times 10^{-12} \text{ m})}{2(654.2 \times 10^{-9})}\right)^2 \left[\frac{(47.95 \text{ u})(1.661 \times 10^{-27} \text{ kg u}^{-1})}{2(1.381 \times 10^{-23} \text{ J K}^{-1})\ln 2}\right]$$

$$T = \boxed{8.34 \times 10^5 \text{ K}}$$

P9.32 See Figure 9.5.

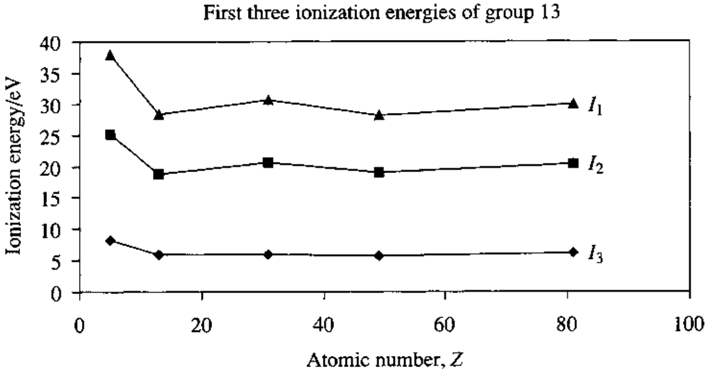


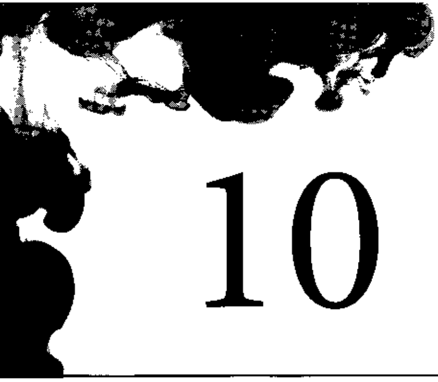
Figure 9.5

Trends:

(i) $I_1 < I_2 < I_3$ because of decreased nuclear shielding as each successive electron is removed.

(ii) The ionization energies of boron are much larger than those of the remaining group elements because the valence shell of boron is very small and compact, with little nuclear shielding. The boron atom is much smaller than the aluminium atom.

(iii) The ionization energies of Al, Ga, In, and Tl are comparable even though successive valence shells are further from the nucleus because the ionization energy decrease expected from large atomic radii is balanced by an increase in effective nuclear charge.



10 Molecular structure

Answers to discussion questions

D10.2 Consider the case of the carbon atom. Mentally, we break the process of hybridization into two major steps. The first is promotion, in which we imagine that one of the electrons in the 2s orbital of carbon ($2s^22p^2$) is promoted to the empty 2p orbital giving the configuration $2s2p^3$. (Note: This promotion is *imaginary*; there is no actual promotion of an electron from a filled 2s orbital into an empty 2p orbital.) In the second step we mathematically mix the four orbitals by way of the specific linear combinations in eqn 10.3 corresponding to the sp^3 hybrid orbitals. The number of orbitals is conserved. If we mix four unhybridized atomic orbitals we must end up with four hybrid orbitals. In the construction of the sp^2 hybrids we start with the 2s orbital and two of the 2p orbitals, and after mixing we end up with three sp^2 hybrid orbitals. In the sp case we start with the 2s orbital and one of the 2p orbitals. The justification for all of this is in a sense the first law of thermodynamics. Energy is a state function and therefore its value is determined only by the final state of the system, not by the path taken to achieve that state, and the path can even be imaginary.

D10.4 See Section 10.1 and *Justification* 10.1 for details on spin pairing in the valence bond (VB) theory. In the VB approach to H_2, two expressions were contemplated for the part of the wavefunction that depends on spatial coordinates, namely $A(1)B(2) + A(2)B(1)$ and $A(1)B(2) - A(2)B(1)$. The former has the lower energy. The Pauli principle requires the total wavefunction to be antisymmetric with respect to interchange of the electrons' labels. The spin factor that goes with the lower-energy spatial factor is $\alpha(1)\beta(2) - \alpha(2)\beta(1)$. This spin wavefunction requires the two electrons to be in *different* spin states (i.e. their spins are paired). This is a side-effect of the lower-energy spatial portion of the wavefunction being *symmetric* with respect to interchange. This side-effect is true of simple VB wavefunctions in general.

In the molecular orbital approach, spin pairing is common, but not ubiquitous. (The paramagnetism of O_2, which is correctly predicted by molecular orbital (MO) theory, is a well-known example of unpaired spins.) Here, the spin-pairing comes from the non-degeneracy of σ molecular orbitals. If two electrons occupy the *same* orbital (whether atomic or molecular), the Pauli principle requires their spins to be different (i.e. paired). Valence electrons only occupy *different* orbitals when those orbitals are degenerate. So in MO theory, we have unpaired electrons only if we have an odd number of electrons or if the highest occupied orbitals are π (or δ, etc.) MOs.

D10.6 These are all terms originally associated with the Hückel approximation used in the treatment of conjugated π electron molecules, in which the π electrons are considered independent of the σ electrons. π-electron binding energy is the sum of the energies of each π electron in the molecule. The delocalization energy is the difference in energy between the conjugated molecule with n double bonds and the energy of n ethene molecules, each of which has one double bond. The π-bond formation energy is the energy released when a π bond is formed. It is obtained from the total π-electron binding energy by subtracting the contribution from the Coulomb integrals, α.

D10.8 See Section 10.7(a). A Hartree–Fock (HF) wavefunction for a closed-shell species that has N_e electrons is a Slater determinant (eqn 10.54) of $N_e/2$ distinct one-electron molecular orbitals (MOs), ψ_m, each doubly occupied. The HF equations [10.55] for the MOs are a set of one-electron Schrödinger equations. Each HF Hamiltonian contains a term for the kinetic energy of the electron, terms for the attraction of the electron to each of the species' nuclei, and terms for the repulsion of the electron from each of the other electrons (both direct Coulombic repulsion and electron-exchange terms that represent spin-correlation effects); see *Further Information* 10.1. The Coulomb and exchange portions of each HF Hamiltonian need the MOs occupied by the *other* electrons of the species: in other words, to solve for any MO, we need to know the other MOs. The HF method circumvents this difficulty by using initial guesses for the MOs as part of the Hamiltonians, using the Hamiltonians to find improved estimates of the MOs, and putting those MOs back into the Hamiltonians for another round of solutions; this iterative procedure is followed until the MOs converge. Finally, the form of the MOs is typically a linear combination of atomic orbitals (LCAO-MO, eqn 10.56). Solving for the MOs, then, amounts to finding the optimal coefficients of the LCAO-MOs by means of the variation principle. The atomic orbitals in an LCAO-MO are called the basis set. Selection of the basis set (i.e. how many functions and of what form) can influence the amount of computational time needed to obtain an HF wavefunction as well as the quality of the result.

Solutions to exercises

E10.1(b) Let A and B represent H1s atomic orbitals centred on the two different H nuclei. Labelling the two different O nuclei C and D, we let C_x and C_z represent two different O2p orbitals centered on O nucleus C, etc. Then, the (unnormalized) spatial portion of wavefunction (for the bonding electrons only) would be

$$\psi = \boxed{\underset{\text{H}_\text{A}\text{–O}_\text{C}\text{ bond}}{\{A(1)C_x(2)+A(2)C_x(1)\}} \times \underset{\text{O–O bond}}{\{C_z(3)D_z(4)+C_z(4)D_z(3)\}} \times \underset{\text{H}_\text{B}\text{–O}_\text{D}\text{ bond}}{\{B(5)D_x(6)+B(6)D_x(5)\}}}$$

Note that there are other possible correct answers. For example, the two O2p orbitals in the O–O bond term must have the same orientation (e.g. p_z orbitals by convention); however, the O2p orbitals in the two different O–H bonds need not have the same orientation (although they must be different from the orbitals in the O–O bond). Also, the numbering of the electrons need not be exactly as shown here: two different electron labels must appear in each linear combination (i.e. in each bond); *within* each bond, the two labels must be interchanged.

COMMENT. This simple VB function embodies two perfectly covalent O–H bonds and one O–O bond. The H–O–O bond angles would be 90° because that is the angle that the O2p orbitals make.

Question. Write a VB spatial wavefunction using sp^3 hybrid orbitals on the oxygens.

E10.2(b) Let s represent the H1s atomic orbital and p_z an F2p orbital centered on the F nucleus. Then, the spatial portion of wavefunction (for the bonding electrons only) would be

$$s(1)p_z(2)+s(2)p_z(1)$$

The spatial factor is symmetric with respect to interchange of the electrons' labels, so the spin factor must be antisymmetric:

$$\alpha(1)\beta(2)-\alpha(2)\beta(1).$$

So, the total (unnormalized) wavefunction for this bond would be

$$\psi=\boxed{\{s(1)p_z(2)+s(2)p_z(1)\}\times\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}}$$

COMMENT. This simple VB function embodies a perfectly covalent H–F bond.

E10.3(b) Let A, B, and C represent appropriately oriented F2p atomic orbitals centred on the three different F nuclei, and h_1, h_2, and h_3 represent the three hybrid sp^2 orbitals on B. Then, the (unnormalized) spatial portion of wavefunction (for the bonding electrons only) would be

$$\psi=\boxed{\{A(1)h_1(2)+A(2)h_1(1)\}\times\{B(3)h_2(4)+B(4)h_2(3)\}\times\{C(5)h_3(6)+C(6)h_3(5)\}}$$

COMMENT. This simple VB function embodies three perfectly covalent B–F bonds involving the same B nucleus.

Question. This wavefunction does not include terms for the lone-pair electrons on the F atoms. Would the basis used for this exercise treat the lone-pair orbitals equivalently? What kind of fluorine orbitals *would* treat the lone pairs equivalently? Repeat this exercise using such a basis.

E10.4(b)

$$h_2=\mathrm{s}+\left(\frac{3}{2}\right)^{1/2}\mathrm{p}_x-\left(\frac{1}{2}\right)^{1/2}\mathrm{p}_y\quad\text{and}\quad h_3=\mathrm{s}-\left(\frac{3}{2}\right)^{1/2}\mathrm{p}_x-\left(\frac{1}{2}\right)^{1/2}\mathrm{p}_y$$

We need to evaluate

$$\int h_2h_3\,\mathrm{d}\tau=\int\left\{\mathrm{s}+\left(\frac{3}{2}\right)^{1/2}\mathrm{p}_x-\left(\frac{1}{2}\right)^{1/2}\mathrm{p}_y\right\}\left\{\mathrm{s}-\left(\frac{3}{2}\right)^{1/2}\mathrm{p}_x-\left(\frac{1}{2}\right)^{1/2}\mathrm{p}_y\right\}\mathrm{d}\tau$$

We assume that the basis atomic orbitals are normalized and mutually orthogonal. We expand the integrand, noting that all cross terms integrate to zero (because the basis orbitals are orthogonal). The remaining terms integrate to one, yielding

$$\int h_2h_3\,\mathrm{d}\tau=\int \mathrm{s}^2\,\mathrm{d}\tau-\frac{3}{2}\int \mathrm{p}_x^2\,\mathrm{d}\tau+\frac{1}{2}\int \mathrm{p}_y^2\,\mathrm{d}\tau=1-\frac{3}{2}+\frac{1}{2}=0$$

E10.5(b) Refer to Figure 10.24 of the text for H_2^- and 10.33 for the others. Place two of the valence electrons in each orbital starting with the lowest-energy orbital, until all valence electrons are used up. Apply Hund's rule to the filling of degenerate orbitals.

(a) H_2^- (3 electrons) $\boxed{1\sigma_g^2 1\sigma_u^1,\ b=0.5}$

(b) N_2 (10 electrons) $\boxed{1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2,\ b=3}$

(c) O_2 (12 electrons) $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2,\ b=2}$

E10.6(b) Refer to Figure 10.33 of the text. ClF is isoelectronic with F_2 and CS with N_2; note, however, that the σ and π orbitals no longer have u or g symmetry, so they are simply labelled consecutively for these molecules.

(a) ClF (14 electrons) $\boxed{1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^4}$

(b) CS (10 electrons) $\boxed{1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2}$

(c) O_2^- (13 electrons) $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^3}$

E10.7(b) Decide whether the electron added or removed increases or decreases the bond order. The simplest procedure is to decide whether the orbital involved (i.e. the one *to which* an electron is added or *from which* one is taken) is a bonding or antibonding orbital. We can draw up the following table, which denotes the orbital involved, using a * to denote antibonding orbitals:

	N_2	NO	O_2	C_2	F_2	CN
(a) AB^-	$1\pi_g^*$	$2\pi^*$	$1\pi_g^*$	$2\sigma_g$	$2\sigma_u^*$	3σ
Change in bond order	−1/2	−1/2	−1/2	+1/2	−1/2	+1/2
(b) AB^+	$2\sigma_g$	$2\pi^*$	$1\pi_g^*$	$1\pi_u$	$1\pi_g^*$	3σ
Change in bond order	−1/2	+1/2	+1/2	−1/2	+1/2	−1/2

(a) Therefore, $\boxed{C_2 \text{ and CN}}$ are stabilized (have lower energy) by anion formation.

(b) $\boxed{\text{NO, } O_2\text{, and } F_2}$ are stabilized by cation formation; in each of these cases the bond order increases.

E10.8(b) Figure 10.1 here is based on Figure 10.32 of the text but with Cl orbitals lower than Br orbitals.

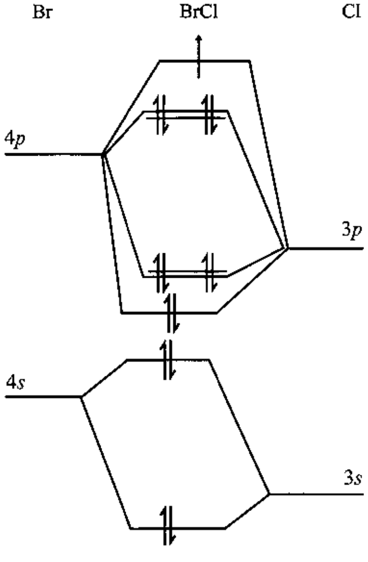


Figure 10.1

For BrCl we insert 14 valence electrons. The bond order is decreased when $BrCl^-$ is formed from BrCl because an electron is added to an antibonding orbital, therefore BrCl will have a shorter bond length than $BrCl^-$.

E10.9(b)

O_2^+ (11 electrons)	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^1$	$b = 2.5$
O_2 (12 electrons)	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$	$b = 2$
O_2^- (13 electrons)	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^3$	$b = 1.5$
O_2^{2-} (14 electrons)	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4$	$b = 1$

Each electron added to O_2^+ is added to an antibonding orbital, thus increasing the length. So, the sequence $\boxed{O_2^+, O_2, O_2^-, O_2^{2-}}$ has progressively longer bonds.

E10.10(b) Normalization requires

$$\int \psi^2\,d\tau = 1 = N^2 \int (\psi_A + \lambda\psi_B)^2\,d\tau = N^2 \int (\psi_A^2 + \lambda^2\psi_B^2 + 2\lambda\psi_A\psi_B)\,d\tau$$

Use the normalization of the basis functions and the definition of the overlap integral (eqn 10.18):

$$\int \psi^2\,d\tau = 1 = N^2(1 + \lambda^2 + 2\lambda S)$$

Hence, $N = \boxed{\left(\dfrac{1}{1 + 2\lambda S + \lambda^2}\right)^{1/2}}$

E10.11(b) We seek an orbital of the form $aA + bB$, where a and b are constants, which is orthogonal to the orbital $N(0.145A + 0.844B)$. Orthogonality requires

$$\int (aA + bB)N(0.145A + 0.844B)\,d\tau = 0$$

$$N\int \{0.145aA^2 + (0.145b + 0.844a)AB + 0.844bB^2\}\,d\tau = 0$$

The integrals of squares of orbitals are 1 and the integral $\int AB\,d\tau$ is the overlap integral S (eqn 10.18), so

$$0 = (0.145 + 0.844S)a + (0.145S + 0.844)b, \quad \text{so} \quad a = \boxed{-\frac{0.145S + 0.844}{0.145 + 0.844S}b}$$

This would make the orbitals orthogonal, but not necessarily normalized. If $S = 0$, the expression simplifies to

$$a = -\frac{0.844}{0.145}b$$

and the new orbital would be normalized if $a = 0.844N$ and $b = -0.145N$. That is

$$\boxed{N(0.844A - 0.145B)}$$

E10.12(b) Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of it overcomes the binding energy (ionization energy) and the remainder is manifest as the kinetic energy of the now freed electron.

$$E_{\text{photon}} = I + E_{\text{kinetic}}$$

$$\text{so}\quad E_{\text{kinetic}} = E_{\text{photon}} - I = \frac{hc}{\lambda} - I = \frac{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{8}\,\text{m s}^{-1})}{(584\times10^{-12}\,\text{m})\times(1.602\times10^{-19}\,\text{J eV}^{-1})} - 4.69\,\text{eV}$$

$$= \boxed{211\overline{9}\,\text{eV}}$$

$$= \boxed{3.39\times10^{-16}\,\text{J}}$$

E10.13(b) $E_{\text{photon}} = I + E_{\text{kinetic}}$ [Exercise 10.12(b)]

The energy of He(I) photons is 21.22 eV [Section 10.4(e)]

$$I = E_{\text{photon}} - E_{\text{kinetic}} = E_{\text{photon}} - \frac{m_e v^2}{2}$$

$$= 21.22\,\text{eV} - \frac{(9.11\times10^{-31}\,\text{kg})\times\{0.00501\times(2.998\times10^{8}\,\text{m s}^{-1})\}^2}{2\times(1.602\times10^{-19}\,\text{J eV}^{-1})}$$

$$= \boxed{14.81\,\text{eV}}$$

$$= \boxed{2.372\times10^{-18}\,\text{J}}$$

E10.14(b) We use results derived in Section 10.5(c) for heteronuclear molecules and no overlap of atomic orbitals. The energies of the molecular orbitals are

$$E_{\pm} = \left(\frac{\alpha_{\text{O}} + \alpha_{\text{Xe}}}{2}\right) \pm \left(\frac{\alpha_{\text{O}} - \alpha_{\text{Xe}}}{2}\right)\left\{1 + \left(\frac{2\beta}{\alpha_{\text{O}} - \alpha_{\text{Xe}}}\right)^2\right\}^{1/2} \quad [10.32\text{c}]$$

Taking the Coulomb integrals to be equal in magnitude and opposite in sign to the ionization energies, we have

$$E_{\pm}/\text{eV} = \left(\frac{-13.6 + (-12.1)}{2}\right) \pm \left(\frac{-13.6 + 12.1}{2}\right)\left\{1 + \left(\frac{2\times(-1.2)}{-13.6 + 12.1}\right)^2\right\}^{1/2}$$

$$\text{so}\quad E_{+} = \boxed{-14.3\,\text{eV}} \quad\text{and}\quad E_{-} = \boxed{-11.4\,\text{eV}}$$

The coefficients are given by eqn 10.38:

$$c_{\text{O}} = \left\{1 + \left(\frac{\alpha_{\text{O}} - E}{\beta}\right)^2\right\}^{-1/2} \quad\text{and}\quad c_{\text{Xe}} = -\left(\frac{\alpha_{\text{O}} - E}{\beta}\right)c_{\text{O}}$$

So, in the bonding orbital

$$c_{\text{O}} = \left\{1 + \left(\frac{-13.6 + 14.3}{-1.2}\right)^2\right\}^{-1/2} = 0.87 \quad\text{and}\quad c_{\text{Xe}} = -\left(\frac{-13.6 + 14.3}{-1.2}\right)\times 0.87 = 0.48$$

and in the antibonding orbital

$$c_O = \left\{1 + \left(\frac{-13.6 + 11.4}{-1.2}\right)^2\right\}^{-1/2} = 0.48 \quad \text{and} \quad c_{Xe} = -\left(\frac{-13.6 + 11.4}{-1.2}\right) \times 0.48 = -0.87$$

Thus, the bonding and antibonding orbitals are, respectively,

$$\psi_+ = \boxed{0.87\chi_O + 0.48\chi_{Xe}} \quad \text{and} \quad \psi_- = \boxed{0.48\chi_O - 0.87\chi_{Xe}}$$

E10.15(b) We use results derived in Section 10.5(c) for heteronuclear molecules with overlap of atomic orbitals. The energies of the molecular orbitals are

$$E_\pm = \frac{\alpha_O + \alpha_{Xe} - 2\beta S}{2(1 - S^2)} \pm \frac{\{(\alpha_O + \alpha_{Xe} - 2\beta S)^2 - 4(1 - S^2)(\alpha_O\alpha_{Xe} - \beta^2)\}^{1/2}}{2(1 - S^2)} \; [10.32a]$$

$$E_\pm/\text{eV} = \frac{-13.6 - 12.1 + 2 \times 1.2 \times 0.20}{2(1 - 0.20^2)}$$

$$\pm \frac{\{(-13.6 - 12.1 + 2 \times 1.2 \times 0.20)^2 - 4(1 - 0.20^2)(13.6 \times 12.1 - 1.2^2)\}^{1/2}}{2(1 - 0.20^2)}$$

Thus, taking the lower energy to be that of the bonding orbital, we have

$$E_{\text{bond}} = \boxed{-14.8\ \text{eV}} \quad \text{and} \quad E_{\text{anti}} = \boxed{-11.5\ \text{eV}}$$

The coefficients are given by eqns 10.36 and 10.34, respectively,

$$c_O = \left\{1 + \left(\frac{\alpha_O - E}{\beta - ES}\right)^2 - 2S\left(\frac{\alpha_O - E}{\beta - ES}\right)\right\}^{-1/2} \quad \text{and} \quad c_{Xe} = -\left(\frac{\alpha_O - E}{\beta - ES}\right)c_O$$

So, in the bonding orbital

$$\frac{\alpha_O - E}{\beta - ES} = \frac{-13.6 + 14.8}{-1.2 + 14.8 \times 0.20} = 0.66,$$

$$c_O = (1 + 0.66^2 - 2 \times 0.20 \times 0.66)^{-1/2} = 0.92 \quad \text{and} \quad c_{Xe} = -0.66 \times 0.92 = -0.61$$

In the antibonding orbital

$$\frac{\alpha_O - E}{\beta - ES} = \frac{-13.6 + 11.5}{-1.2 + 11.5 \times 0.20} = -1.8\overline{9},$$

$$c_O = (1 + 1.8\overline{9}^2 + 2 \times 0.20 \times 1.8\overline{9})^{-1/2} = 0.43 \quad \text{and} \quad c_{Xe} = 1.8\overline{9} \times 0.43 = 0.82$$

Thus, the bonding and antibonding orbitals are, respectively,

$$\psi_{\text{bond}} = \boxed{0.92\chi_O - 0.61\chi_{Xe}} \quad \text{and} \quad \psi_{\text{anti}} = \boxed{0.43\chi_O + 0.82\chi_{Xe}}$$

E10.16(b) The molecular orbitals of the fragments and the molecular oribitals that they form are shown in Figure 10.2.

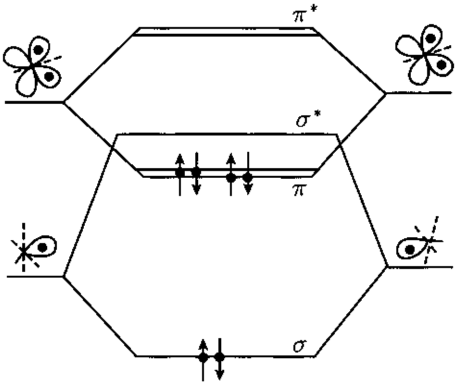


Figure 10.2

E10.17(b) In setting up the secular determinant we use the approximations of Section 10.6:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

The atomic orbital basis consists of unhybridized $2p_z$ orbitals centred on each carbon atom. We ignore overlap between the terminal carbon atoms because they are not neighbouring. To find the energies, expand the determinants:

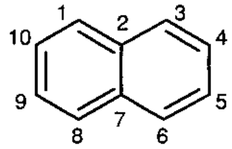
$$(\alpha - E) \times \{(\alpha - E)(\alpha - E) - \beta^2\} - \beta \times \beta(\alpha - E) = 0,$$
$$0 = (\alpha - E) \times \{(\alpha - E)(\alpha - E) - 2\beta^2\} = (\alpha - E)(\alpha - E + 2^{1/2}\beta)(\alpha - E - 2^{1/2}\beta)$$

The roots (the orbital energies) are $E = \alpha,\ \alpha \pm 2^{1/2}\beta$. The binding energy is the sum of the orbital energies of the occupied orbitals:

$$E_\pi = 2(\alpha + 2^{1/2}\beta) + \alpha = \boxed{3\alpha + 2^{3/2}\beta}$$

COMMENT. The secular determinant and the expression for binding energy are formally the same as for linear H_3 (Exercise 10.17(a)). The parameters α and β would have different values, however.

E10.18(b) The structure of naphthalene is numbered to match the row and column numbers shown in the secular determinant.



$$\begin{array}{c|cccccccccc|} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ 1 & \alpha - E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\ 2 & \beta & \alpha - E & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 \\ 3 & 0 & \beta & \alpha - E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & \beta & \alpha - E & \beta & 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 & \beta & \alpha - E & \beta & 0 & 0 & 0 & 0 \\ 6 & 0 & 0 & 0 & 0 & \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 7 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 8 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 9 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha - E & \beta \\ 10 & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha - E \end{array}$$

The secular determinant can be diagonalized with the assistance of general-purpose mathematical software. Alternatively, programs specifically designed for Hückel calculations (such as the Simple Huckel Molecular Orbital Theory Calculator at the University of Calgary, http://www.chem.ucalgary.ca/SHMO/, or Hückel software in *Explorations in Physical Chemistry*, 2nd edn, de Paula, Walters, and Atkins, http://ebooks.bfwpub.com/explorations.php) can be used. Application of such software yields 10 non-degenerate π orbitals, whose 'energies' are given in the following table (What the table actually lists is $(E-\alpha)/\beta$):

Level	1	2	3	4	5
$(E-\alpha)/\beta$	2.303	1.618	1.303	1.000	0.618
Level	6	7	8	9	10
$(E-\alpha)/\beta$	−0.618	−1.000	−1.303	−1.618	−2.303

As usual, we fill the orbitals starting from the lowest energy orbital, obeying the Pauli principle and Hund's rule.

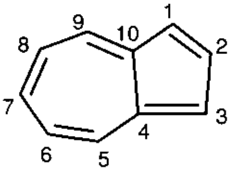
(a) $C_{10}H_8^-$ (11 electrons): $\boxed{1\pi^2 2\pi^2 3\pi^2 4\pi^2 5\pi^2 6\pi^1}$

$$E_\pi = 2(\alpha+2.303\beta)+2(\alpha+1.618\beta)+2(\alpha+1.303\beta)+2(\alpha+\beta)$$
$$+2(\alpha+0.618\beta)+(\alpha-0.618\beta)=\boxed{11\alpha+13.066\beta}$$

(b) $C_{10}H_8^+$ (9 electrons): $\boxed{1\pi^2 2\pi^2 3\pi^2 4\pi^2 5\pi^1}$

$$E_\pi = 2(\alpha+2.303\beta)+2(\alpha+1.618\beta)+2(\alpha+1.303\beta)+2(\alpha+\beta)$$
$$+(\alpha+0.618\beta)=\boxed{9\alpha+13.066\beta}$$

E10.19(b) The structure is numbered to match the row and column numbers shown in the determinants:



$$\begin{array}{c|cccccccccc|}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\
1 & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
2 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
3 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & \beta \\
5 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\
6 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\
7 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\
8 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\
9 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\
10 & \beta & 0 & 0 & \beta & 0 & 0 & 0 & 0 & \beta & \alpha-E
\end{array}$$

Azulene has 10 π electrons, which fill five orbitals. The energies of the filled orbitals are $\alpha+2.310\beta$, $\alpha+1.652\beta$, $\alpha+1.356\beta$, $\alpha+0.887\beta$, and $\alpha+0.477\beta$. Thus, the total π-electron binding energy is $\boxed{10\alpha+13.364\beta}$.

Solutions to problems

Solutions to numerical problems

P10.2 Figure 10.3 is a sketch of an s orbital and a p orbital at various internuclear separations, beginning with zero separation. From these crude sketches, we can anticipate how the overlap integral would vary. At zero separation, the overlap would be zero by symmetry: the overlap of the s orbital with the positive and negative parts of the p orbital are equal and opposite. As the s orbital overlaps the positive lobe of the p orbital, the overlap integral increases. Eventually, however, the orbitals are too far apart for any significant overlap.

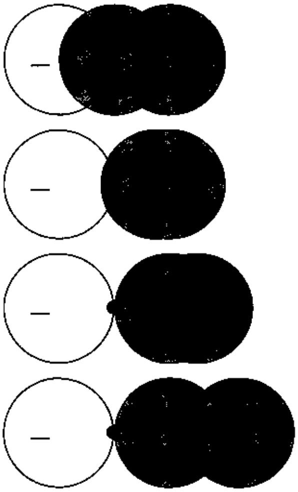


Figure 10.3

The expression given in the text for the overlap integral between a hydrogenic 1s and $2p_z$ orbital is plotted in Figure 10.4. Note that it displays a maximum overlap not when the nuclei are coincident (for there they are orthogonal) but at an intermediate separation.

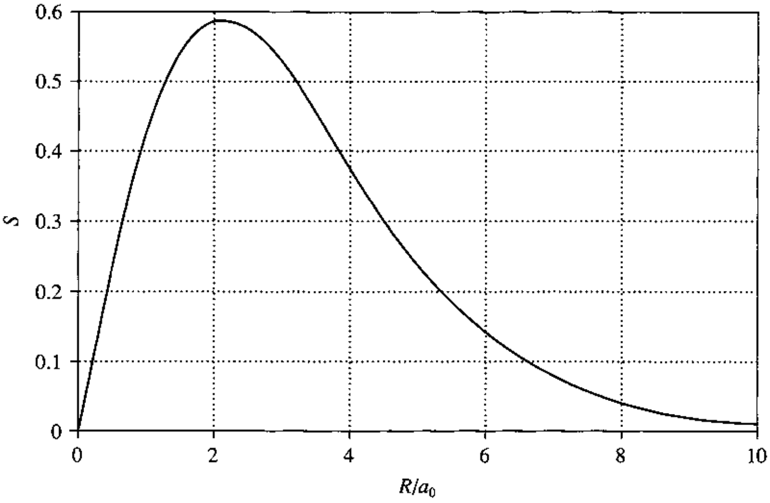


Figure 10.4

From the graph, we can see that maximum overlap occurs at about $R = \boxed{2.1\,a_0}$.

Question. Find the position of maximum overlap analytically by differentiating S and setting the derivative equal to zero.

P10.4 We obtain the electron densities from $\rho_+ = \psi_+^2$ and $\rho_- = \psi_-^2$, with ψ_+ and ψ_- as given in Section 10.3. We then calculate with

$$A = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \mathrm{e}^{-r_A/a_0} \quad \text{and} \quad \psi_\pm = N_\pm\left(\frac{1}{\pi a_0^3}\right)^{1/2}\{\mathrm{e}^{-r_A/a_0} \pm \mathrm{e}^{-r_B/a_0}\}\ [10.9]$$

Measuring both r_A and r_B from nucleus A, along the internuclear line, we have

$$\psi_\pm = N_\pm\left(\frac{1}{\pi a_0^3}\right)^{1/2}\{\mathrm{e}^{-|z|/a_0} \pm \mathrm{e}^{-|z-R|/a_0}\}$$

with z measured from A along the axis toward B. We use the normalization factors from Example 10.1:

$$N_\pm = \left(\frac{1}{2(1 \pm S)}\right)^{1/2}$$

We first calculate the overlap integral, S, at $R = 106\ \text{pm} = 2a_0$.

$$S = \left(1 + 2 + \frac{1}{3}(2)^2\right)\mathrm{e}^{-2} = 0.586\ [10.13a]$$

Then, $$N_+ = \left(\frac{1}{2(1+S)}\right)^{1/2} = \left(\frac{1}{2(1+0.586)}\right)^{1/2} = 0.561$$

$$N_- = \left(\frac{1}{2(1-S)}\right)^{1/2} = \left(\frac{1}{2(1-0.586)}\right)^{1/2} = 1.09\overline{9}$$

Hence, $$\rho_\pm = N_\pm^2\left(\frac{1}{\pi a_0^3}\right)\{\mathrm{e}^{-|z|/a_0} \pm \mathrm{e}^{-|z-R|/a_0}\}^2$$

We evaluate the factors preceding the exponentials in ψ_+ and ψ_-

$$N_+\left(\frac{1}{\pi a_0^3}\right)^{1/2} = 0.561 \times \left(\frac{1}{\pi \times (52.9\ \text{pm})^3}\right)^{1/2} = \frac{1}{1216\ \text{pm}^{3/2}}$$

Likewise, $$N_-\left(\frac{1}{\pi a_0^3}\right)^{1/2} = \frac{1}{621\ \text{pm}^{3/2}}$$

Then, $$\rho_+ = \frac{1}{(1216)^2\ \text{pm}^3}\{\mathrm{e}^{-|z|/a_0} + \mathrm{e}^{-|z-R|/a_0}\}^2$$

and $$\rho_- = \frac{1}{(621)^2\ \text{pm}^3}\{\mathrm{e}^{-|z|/a_0} - \mathrm{e}^{-|z-R|/a_0}\}^2$$

The 'atomic' density is

$$\rho = \frac{1}{2}\{\psi_{1s}(\mathrm{A})^2 + \psi_{1s}(\mathrm{B})^2\} = \frac{1}{2} \times \left(\frac{1}{\pi a_0^3}\right)\{\mathrm{e}^{-2r_\mathrm{A}/a_0} + \mathrm{e}^{-2r_\mathrm{B}/a_0}\}$$

$$= \frac{\mathrm{e}^{-2r_\mathrm{A}/a_0} + \mathrm{e}^{-2r_\mathrm{B}/a_0}}{9.30 \times 10^5\ \mathrm{pm}^3}$$

$$= \frac{\mathrm{e}^{-2|z|/a_0} + \mathrm{e}^{-2|z-R|/a_0}}{9.30 \times 10^5\ \mathrm{pm}^3}$$

The difference density is $\delta\rho_\pm = \rho_\pm - \rho$.

We draw up the following table with $R = 106$ pm and $a_0 = 52.9$ pm:

z/pm	−100	−80	−60	−40	−20	0	20	40
$\rho_+ \times 10^7/\mathrm{pm}^{-3}$	0.20	0.42	0.90	1.92	4.09	8.72	5.27	3.88
$\rho_- \times 10^7/\mathrm{pm}^{-3}$	0.44	0.94	2.01	4.27	9.11	19.40	6.17	0.85
$\rho \times 10^7/\mathrm{pm}^{-3}$	0.25	0.53	1.13	2.41	5.15	10.93	5.47	3.26
$\delta\rho_+ \times 10^7/\mathrm{pm}^{-3}$	−0.05	−0.11	−0.23	−0.49	−1.05	−2.20	−0.20	0.62
$\delta\rho_- \times 10^7/\mathrm{pm}^{-3}$	0.19	0.41	0.87	1.86	3.96	8.47	0.70	−2.40

z/pm	60	80	100	120	140	160	180	200
$\rho_+ \times 10^7/\mathrm{pm}^{-3}$	3.73	4.71	7.42	5.10	2.39	1.12	0.53	0.25
$\rho_- \times 10^7/\mathrm{pm}^{-3}$	0.25	4.02	14.41	11.34	5.32	2.50	1.17	0.55
$\rho \times 10^7/\mathrm{pm}^{-3}$	3.01	4.58	8.88	6.40	3.00	1.41	0.66	0.31
$\delta\rho_+ \times 10^7/\mathrm{pm}^{-3}$	0.70	0.13	−1.46	−1.29	−0.61	−0.29	−0.14	−0.06
$\delta\rho_- \times 10^7/\mathrm{pm}^{-3}$	−2.76	−0.56	5.54	4.95	2.33	1.09	0.51	0.24

The densities are plotted in Figure 10.5(a) and the difference densities are plotted in Figure 10.5(b).

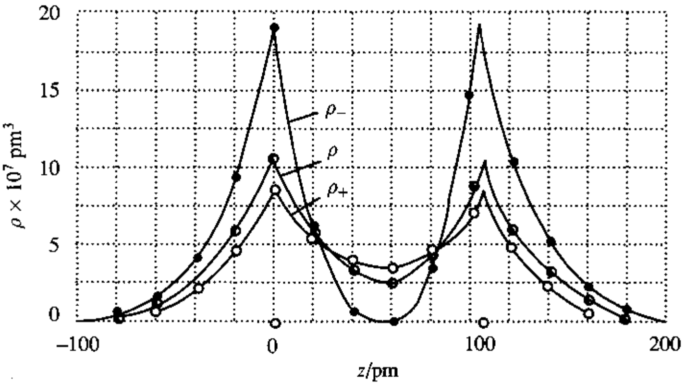


Figure 10.5(a)

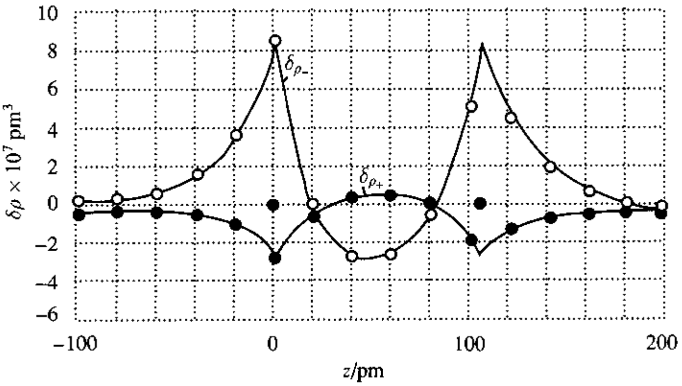


Figure 10.5(b)

P10.6 $P = |\psi|^2\,\mathrm{d}\tau \approx |\psi|^2\,\delta\tau,\ \delta\tau = 1.00\ \text{pm}^3$

(a) From Problem 10.4

$\psi_+^2(z=0) = \rho_+(z=0) = 8.7 \times 10^{-7}\ \text{pm}^{-3}$

Therefore, the probability of finding the electron in the volume $\delta\tau$ at nucleus A is

$P = 8.6 \times 10^{-7}\ \text{pm}^{-3} \times 1.00\ \text{pm}^3 = \boxed{8.6 \times 10^{-7}}$

(b) By symmetry (or by taking $z = 106$ pm), $P = \boxed{8.6 \times 10^{-7}}$.

(c) From Figure 10.5(a), $\psi_+^2(\tfrac{1}{2}R) = 3.7 \times 10^{-7}\ \text{pm}^{-3}$, so $P = \boxed{3.7 \times 10^{-7}}$.

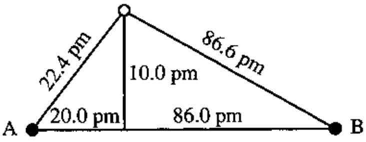


Figure 10.6

(d) From Figure 10.6, the point referred to lies at 22.4 pm from A and 86.6 pm from B.

Therefore, $\psi_+ = \dfrac{\mathrm{e}^{-22.4/52.9} + \mathrm{e}^{-86.6/52.9}}{1216\ \text{pm}^{3/2}} = \dfrac{0.65 + 0.19}{1216\ \text{pm}^{3/2}} = 6.98 \times 10^{-4}\,\text{pm}^{-3/2}$

$\psi_+^2 = 4.9 \times 10^{-7}\ \text{pm}^{-3}$, so $P = \boxed{4.9 \times 10^{-7}}$

For the antibonding orbital, we proceed similarly.

(a) $\psi_-^2(z=0) = 19.4 \times 10^{-7}\ \text{pm}^{-3}$ [Problem 10.4], so $P = \boxed{2.0 \times 10^{-6}}$

(b) By symmetry, $P = \boxed{2.0 \times 10^{-6}}$

(c) $\psi_-^2(\tfrac{1}{2}R) = 0$, so $P = \boxed{0}$

(d) We evaluate ψ_- at the point specified in Figure 10.6:

$$\psi_- = \frac{0.65 - 0.19}{621\ \text{pm}^{3/2}} = 7.41 \times 10^{-4}\ \text{pm}^{-3/2}$$

$$\psi_-^2 = 5.49 \times 10^{-7}\ \text{pm}^{-3}, \quad \text{so} \quad P = \boxed{5.5 \times 10^{-7}}$$

P10.8 Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of that energy overcomes the binding energy of the electron (ionization energy) and the remainder is manifest as the kinetic energy of the now freed electron.

$$E_{\text{photon}} = I + E_{\text{kinetic}}, \quad \text{so} \quad I = E_{\text{photon}} - E_{\text{kinetic}}$$

so the first three ionization energies are:

$$I_1 = 21.21\ \text{eV} - 11.01\ \text{eV} = \boxed{10.20\ \text{eV}}$$

$$I_2 = 21.21\ \text{eV} - 8.23\ \text{eV} = \boxed{12.98\ \text{eV}}$$

and $I_3 = 21.21\ \text{eV} - 5.22\ \text{eV} = \boxed{15.99\ \text{eV}}$

Figure 10.7 displays the energy level diagram.

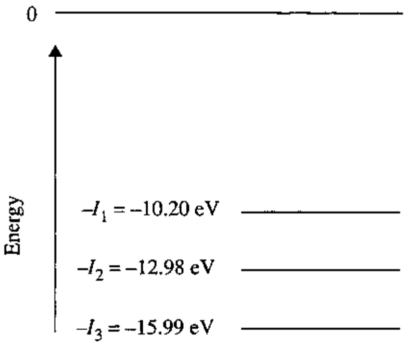


Figure 10.7

P10.10 $E_n = \dfrac{n^2h^2}{8mL^2}$, $n = 1, 2, \ldots$ and $\psi_n = \left(\dfrac{2}{L}\right)^{1/2} \sin\left(\dfrac{n\pi x}{L}\right)$ [Section 8.1]

Two electrons occupy each level (by the Pauli principle), and so butadiene (in which there are four π electrons) has two electrons in ψ_1 and two electrons in ψ_2:

$$\psi_1 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \quad \text{and} \quad \psi_2 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{2\pi x}{L}\right)$$

These orbitals are sketched in Figure 10.8(a).

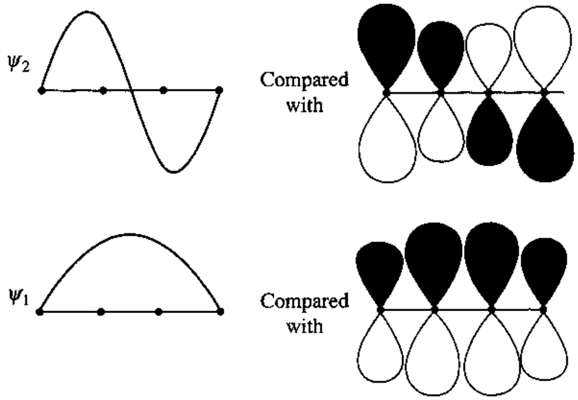


Figure 10.8(a)

The minimum excitation energy is

$$\Delta E = E_3 - E_2 = 5\left(\frac{h^2}{8m_eL^2}\right)$$

In $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$ there are eight π electrons to accommodate, so the HOMO will be ψ_4 and the LUMO ψ_5. From the particle-in-a-box solutions

$$\begin{aligned}\Delta E = E_5 - E_4 &= (25-16)\frac{h^2}{8m_eL^2} = \frac{9h^2}{8m_eL^2}\\ &= \frac{(9)\times(6.626\times10^{-34}\ \mathrm{J\ s})^2}{(8)\times(9.109\times10^{-31}\ \mathrm{kg})\times(1.12\ \times10^{-9}\ \mathrm{m})^2}\\ &= 4.3\times10^{-19}\ \mathrm{J}\end{aligned}$$

which corresponds to $\boxed{2.7\ \mathrm{eV}}$. The HOMO and LUMO are

$$\psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)$$

with $n = 4$ and 5, respectively; the two wavefunctions are sketched in Figure 10.8(b).

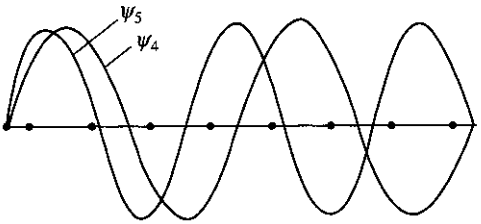


Figure 10.8(b)

COMMENT. It follows that

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{4.3\times10^{-19}\ \text{J}} = 4.6\times10^{-7}\ \text{m}, \quad \text{or} \quad \boxed{460\ \text{nm}}.$$

The wavelength 460 nm corresponds to blue light; so the molecule is likely to appear $\boxed{\text{orange}}$ in white light because blue is subtracted.

P10.12 (a) In the absence of numerical values for α and β, we express orbital energies as $(E_k-\alpha)/\beta$ for the purpose of comparison. Recall that α and β are negative, so the orbital with the greatest value of $(E_k-\alpha)/\beta$ has the lowest energy. Draw up the following table, evaluating

$$\frac{E_k-\alpha}{\beta} = 2\cos\frac{2k\pi}{N}$$

	Energy $(E_k-\alpha)/\beta$	
Orbital, k	C_6H_6	C_8H_8
±4		−2.000
±3	−2.000	−1.414
±2	−1.000	0
±1	1.000	1.414
0	2.000	2.000

In each case, the lowest and highest energy levels are non-degenerate, while the other energy levels are doubly degenerate. The degeneracy is clear for all energy levels except, perhaps, the highest: each value of the quantum number k corresponds to a separate MO, and positive and negative values of k therefore give rise to a pair of MOs of the same energy. This is not the case for the highest energy level, however, because there are only as many MOs as there were atomic orbitals (AOs) input to the calculation, which is the same as the number of carbon atoms; having a doubly degenerate top energy level would yield one extra MO.

(b) The total energy of the π electron system is the sum of the energies of occupied orbitals weighted by the number of electrons that occupy them. In C_6H_6, each of the first three orbitals is doubly occupied, but the second level ($k=\pm1$) is doubly degenerate, so

$$E_\pi = 2E_0 + 2\times 2E_1 = 2(\alpha+2\beta\cos 0) + 4\left(\alpha+2\beta\cos\frac{2\pi}{6}\right) = 6\alpha+8\beta$$

The delocalization energy is the difference between this quantity and that of three isolated double bonds:

$$E_{\text{deloc}} = E_\pi - 6(\alpha+\beta) = 6\alpha+8\beta-6(\alpha+\beta) = \boxed{2\beta}$$

For linear hexatriene, $E_{\text{deloc}} = \boxed{0.988\beta}$, so benzene has considerably more delocalization energy (assuming that β is similar in the two molecules). This extra stabilization is an example of the special stability of $\boxed{\text{aromatic}}$ compounds.

(c) In C_8H_8, each of the first three orbitals is doubly occupied, but the second level ($k = \pm 1$) is doubly degenerate. The next level is also doubly degenerate, with a single electron occupying each orbital. So, the energy is

$$\begin{aligned} E_\pi &= 2E_0 + 2\times 2E_1 + 2\times 1E_2 \\ &= 2(\alpha + 2\beta\cos 0) + 4\left(\alpha + 2\beta\cos\frac{2\pi}{8}\right) + 2\left(\alpha + 2\beta\cos\frac{4\pi}{8}\right) \\ &= 8\alpha + 9.657\beta \end{aligned}$$

The delocalization energy is the difference between this quantity and that of four isolated double bonds:

$$E_{\text{deloc}} = E_\pi - 8(\alpha + \beta) = 8\alpha + 9.657\beta - 8(\alpha + \beta) = \boxed{1.657\beta}$$

This delocalization energy is not much different from that of linear octatetraene ($\boxed{1.518\beta}$), so cyclooctatetraene does not have much additional stabilization over the linear structure. Once again, however, we do see that the delocalization energy stabilizes the π orbitals of the closed-ring conjugated system to a greater extent than what is observed in the open-chain conjugated system. However, the benzene/hexatriene comparison shows a much greater stabilization than does the cyclooctatetraene/octatetraene system. This is a demonstration of the Hückel $4n + 2$ rule, which states that any planar, cyclic, conjugated system exhibits unusual aromatic stabilization if it contains $4n + 2$ π electrons, where n is an integer (but not a quantum number). Benzene with its 6 π electrons has this aromatic stabilization, whereas cycloctatetraene with 8 π electrons doesn't have this unusual stabilization. We can say that it is $\boxed{\text{not aromatic}}$, consistent with indicators of aromaticity such as the Hückel $4n + 2$ rule.

P10.14 See Figure 10.9. In all of the molecules considered, the HOMO is bonding with respect to the carbon atoms connected by double bonds, but antibonding with respect to the carbon atoms connected by single bonds. (The bond lengths returned by the modelling software suggest that it makes sense to talk about double bonds and single bonds. Despite the electron delocalization, the nominal double bonds are consistently shorter than the nominal single bonds.) The LUMO had just the opposite character, tending to weaken the C=C bonds but strengthen the C–C bonds. To arrive at this conclusion, examine the nodal surfaces of the orbitals. An orbital has an antibonding effect on atoms between which nodes occur, and it has a binding effect on atoms that lie within regions in which the orbital does not change sign. The $\pi^* \leftarrow \pi$ transition, then, would lengthen and weaken the double bonds and shorten and strengthen the single bonds, bringing the different kinds of polyene bonds closer to each other in length and strength. Since each molecule has more double bonds than single bonds, there is an overall weakening of bonds. (See Figure 10.9.)

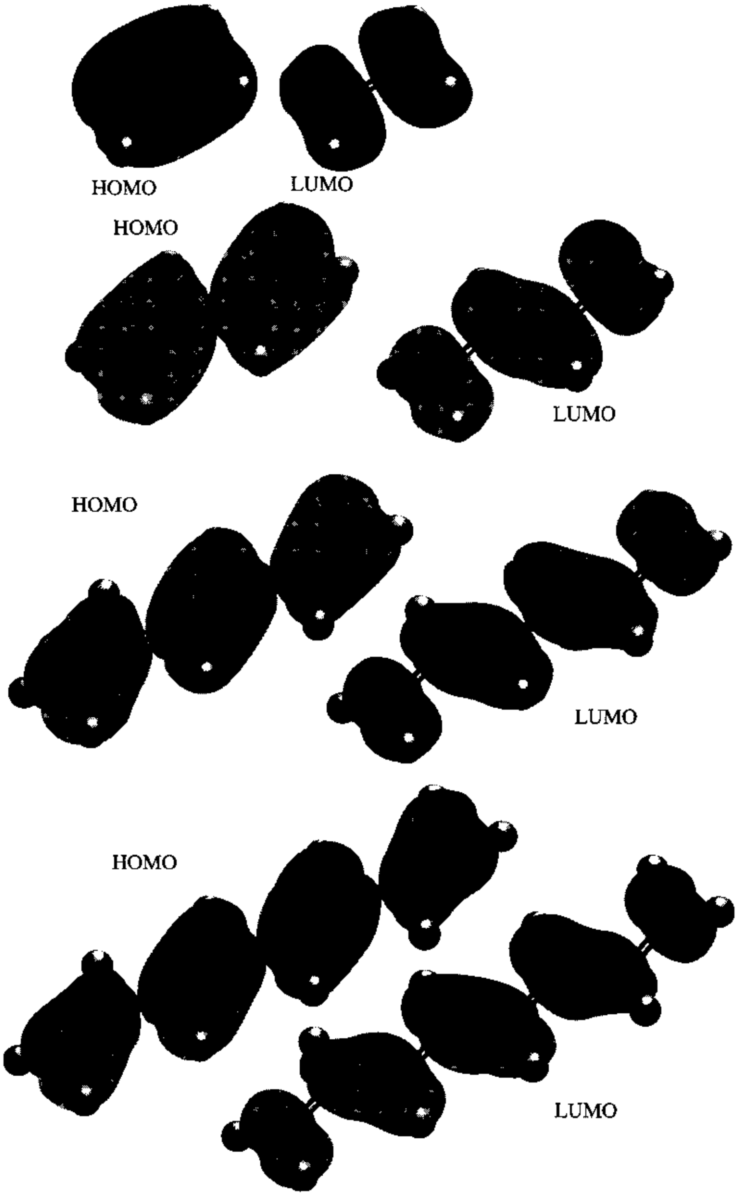


Figure 10.9

Solutions to theoretical problems

P10.16 The explicit form of the h_2 sp^2 hybrid is

$$h_2 = \mathrm{s} + \left(\frac{3}{2}\right)^{1/2} \mathrm{p}_x - \left(\frac{1}{2}\right)^{1/2} \mathrm{p}_y \; [10.5]$$

The unhybridized orbitals are put together from the radial and angular functions listed in Tables 9.1 and 8.2:

$$2\text{s} = R_{20}Y_{00} = \frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \times (2-\rho)\text{e}^{-\rho/2} \times \left(\frac{1}{4\pi}\right)^{1/2} = \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)\text{e}^{-\rho/2}$$

$$2\text{p}_x = -\frac{1}{2^{1/2}}R_{21}(Y_{1,+1} - Y_{1,-1})\ [9.22]$$

$$= -\frac{1}{2^{1/2}} \times \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho\text{e}^{-\rho/2} \times \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta(-\text{e}^{+\text{i}\phi} - \text{e}^{-\text{i}\phi})$$

$$= \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\rho\text{e}^{-\rho/2}\sin\theta\cos\phi$$

$$2\text{p}_y = \frac{\text{i}}{2^{1/2}}R_{21}(Y_{1,+1} + Y_{1,-1})\ [9.22]$$

$$= \frac{\text{i}}{2^{1/2}} \times \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho\text{e}^{-\rho/2} \times \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta(-\text{e}^{+\text{i}\phi} + \text{e}^{-\text{i}\phi})$$

$$= \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\rho\text{e}^{-\rho/2}\sin\theta\sin\phi$$

where $\rho = \dfrac{2Zr}{2a} = \dfrac{Zr}{a}$

In forming the hybrid, pull out the factor of $\left(\dfrac{1}{32\pi}\right)^{1/2}\left(\dfrac{Z}{a}\right)^{3/2}\text{e}^{-\rho/2}$ common to each component:

$$h_2 = \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\text{e}^{-\rho/2}\left\{2 - \rho + \left(\frac{3}{2}\right)^{1/2}\rho\sin\theta\cos\phi - \left(\frac{1}{2}\right)^{1/2}\rho\sin\theta\sin\phi\right\}$$

$$= \left(\frac{1}{32\pi}\right)\left(\frac{Z}{a}\right)^{3/2}\text{e}^{-\rho/2}\left\{2 + \rho\left(\frac{3^{1/2}\cos\phi - \sin\phi}{2^{1/2}}\sin\theta - 1\right)\right\}$$

To find the angles at which h_2 has maximum amplitude, differentiate with respect to angles:

$$\frac{\partial h_2}{\partial\phi} = 0 = \left(\frac{1}{32\pi}\right)\left(\frac{Z}{a}\right)^{3/2}\text{e}^{-\rho/2}\left(\frac{\rho\sin\theta}{2^{1/2}}\right)(-3^{1/2}\sin\phi - \cos\phi)$$

so $\dfrac{\sin\phi}{\cos\phi} = -\dfrac{1}{3^{1/2}} = \tan\phi$ or $\phi = 5\pi/6$ or $11\pi/6$ (150° or 330°).

Evaluating the functions at these angles shows that $\dfrac{3^{1/2}\cos\phi - \sin\phi}{2^{1/2}}\sin\theta - 1$ has a positive maximum at $\phi = 11\pi/6$ and a negative minimum at $5\pi/6$. Recall that the sign of an orbital or wavefunction does not matter; the direction of maximum amplitude is the one where h_2^2 is greatest. For this function, that corresponds to $\boxed{11\pi/6\ (330°)}$, the positive maximum, because the terms that depend on angles then add to positive constants rather than diminish them. Differentiating with respect to θ yields

$$\frac{\partial h_2}{\partial\theta}=0=\left(\frac{1}{32\pi}\right)\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}\left(\frac{3^{1/2}\cos\phi-\sin\phi}{2^{1/2}}\right)\cos\theta$$

so $\theta=\pi/2$ (90°). Thus, the orbital has its maximum amplitude in the xy plane, as expected.

P10.18 The LCAO-MOs are

$\psi_{\pm}=N_{\pm}(A\pm B)$ [10.8]

with $N_{\pm}^2=\dfrac{1}{2(1\pm S)}$ [Example 10.1]

The Hamiltonian is

$$H=-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_A}-\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_B}+\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{R}\,[10.7]=-\frac{\hbar^2}{2m}\nabla^2-\frac{j_0}{r_A}-\frac{j_0}{r_B}+\frac{j_0}{R}$$

where we have introduced the abbreviation $j_0=\dfrac{e^2}{4\pi\varepsilon_0}$.

$H\psi=E\psi$ implies that

$$-\frac{\hbar^2}{2m}\nabla^2\psi-\frac{j_0}{r_A}\psi-\frac{j_0}{r_B}\psi+\frac{j_0}{R}\psi=E\psi$$

Multiply through by ψ^* (which is equal to ψ) and integrate using

$$\left.\begin{array}{l}-\dfrac{\hbar^2}{2m}\nabla^2A-\dfrac{j_0}{r_A}A=E_HA\\[2ex]-\dfrac{\hbar^2}{2m}\nabla^2B-\dfrac{j_0}{r_B}B=E_HB\end{array}\right.\qquad[A\text{ and }B\text{ are solutions for the H atom}]$$

Let's work first with ψ_+:

$$N_+\int\psi_+\left(E_HA+E_HB-\frac{j_0}{r_A}B-\frac{j_0}{r_B}A+\frac{j_0}{R}(A+B)\right)d\tau=E_+$$

hence, $$E_H\int\psi_+^2\,d\tau+\frac{j_0}{R}\int\psi_+^2\,d\tau-j_0N_+\int\psi_+\left(\frac{B}{r_A}+\frac{A}{r_B}\right)d\tau=E_+$$

and so, $$E_H+\frac{j_0}{R}-j_0N_+^2\int\left(A\frac{B}{r_A}+B\frac{B}{r_A}+A\frac{A}{r_B}+B\frac{A}{r_B}\right)d\tau=E_+$$

Now, use $j_0\displaystyle\int A\frac{B}{r_A}d\tau=j_0\int B\frac{A}{r_B}d\tau$ (by symmetry); call this integral (including the factor of j_0) k.

Similarly

$$j_0\int A\frac{A}{r_B}d\tau=j_0\int B\frac{B}{r_A}d\tau \text{ (by symmetry); call this integral } j.$$

Putting all the terms together, we have

$$E_{\mathrm{H}} + \frac{j_0}{R} - N_+^2 \times 2(j+k) = E_+ = E_{\mathrm{H}} + \frac{j_0}{R} - \frac{j+k}{1+S},$$

which is eqn 10.12.

The analogous expression for E_- is obtained by starting from

$$N_- \int \psi_- \left(E_{\mathrm{H}}A - E_{\mathrm{H}}B + \frac{j_0}{r_{\mathrm{A}}}B - \frac{j_0}{r_{\mathrm{B}}}A + \frac{j_0}{R}(A-B) \right) \mathrm{d}\tau = E_-$$

Following the same steps as above leads to

$$E_- = E_{\mathrm{H}} + \frac{j_0}{R} - \frac{j-k}{1-S},$$

which is eqn 10.15.

P10.20 Differentiate eqn 10.30 with respect to one of the coefficients, say c_{A}. (The steps would be identical for c_{B}.)

$$E = \frac{c_{\mathrm{A}}^2\alpha_{\mathrm{A}} + c_{\mathrm{B}}^2\alpha_{\mathrm{B}} + 2c_{\mathrm{A}}c_{\mathrm{B}}\beta}{c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2 + 2c_{\mathrm{A}}c_{\mathrm{B}}S}$$

Hence, $$\frac{\partial E}{\partial c_{\mathrm{A}}} = \frac{2c_{\mathrm{A}}\alpha_{\mathrm{A}} + 2c_{\mathrm{B}}\beta}{c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2 + 2c_{\mathrm{A}}c_{\mathrm{B}}S} - \frac{c_{\mathrm{A}}^2\alpha_{\mathrm{A}} + c_{\mathrm{B}}^2\alpha_{\mathrm{B}} + 2c_{\mathrm{A}}c_{\mathrm{B}}\beta}{(c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2 + 2c_{\mathrm{A}}c_{\mathrm{B}}S)^2} \times (2c_{\mathrm{A}} + 2c_{\mathrm{B}}S)$$

$$= \frac{2(c_{\mathrm{A}}\alpha_{\mathrm{A}} + c_{\mathrm{B}}\beta)}{c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2 + 2c_{\mathrm{A}}c_{\mathrm{B}}S} - E \times \frac{2c_{\mathrm{A}} + 2c_{\mathrm{B}}S}{c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2 + 2c_{\mathrm{A}}c_{\mathrm{B}}S} = \boxed{2 \times \frac{c_{\mathrm{A}}\alpha_{\mathrm{A}} - c_{\mathrm{A}}E + c_{\mathrm{B}}\beta - c_{\mathrm{B}}SE}{c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2 + 2c_{\mathrm{A}}c_{\mathrm{B}}S}}$$

P10.22 Define a parameter θ by letting

$$(1)\quad \theta = \frac{1}{2}\arctan\left(\frac{2\beta}{\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}}\right);\ \text{thus,}\quad \frac{2\beta}{\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}} = \tan 2\theta$$

Note: $\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}$, not the other way around as in the main text.

We are to prove that the solutions may also be expressed in terms of this parameter more simply as

$$E_+ = \alpha_{\mathrm{A}} + \beta\tan\theta \quad \text{and} \quad E_- = \alpha_{\mathrm{B}} - \beta\tan\theta$$

If these latter expressions are true, then these expressions for E must obey the secular determinant equations. That is,

$$(\alpha_{\mathrm{A}} - E_+)(\alpha_{\mathrm{B}} - E_+) - \beta^2 = 0 \quad \text{and} \quad (\alpha_{\mathrm{A}} - E_-)(\alpha_{\mathrm{B}} - E_-) - \beta^2 = 0$$

Expanding the E_+ equation yields

$$0 = (-\beta\tan\theta)(\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}} - \beta\tan\theta) - \beta^2 = \beta^2\tan^2\theta + (\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})\beta\tan\theta - \beta^2$$

Solving for $\tan\theta$ yields

$$(2)\quad \tan\theta = \frac{(\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}})\beta \pm \sqrt{(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2\beta^2 + 4\beta^4}}{2\beta^2} = \frac{\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}}}{2\beta}\left\{1 \pm \sqrt{1 + \left(\frac{2\beta}{\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}}}\right)^2}\right\}$$

Purely for convenience, define $c = \dfrac{\alpha_B - \alpha_A}{2\beta}$ so $\tan\theta = c\left\{1 \pm \sqrt{1 + \left(\dfrac{1}{c}\right)^2}\right\} = c \pm \sqrt{c^2 + 1}$.

Expanding the E_- equation yields

$$0 = (\alpha_A - \alpha_B + \beta \tan\theta)\beta \tan\theta - \beta^2 = \beta^2 \tan^2\theta + (\alpha_A - \alpha_B)\beta \tan\theta - \beta^2$$

the same equation as before, leading to the definition of $\tan\theta$ in eqn (2) above.

To see whether the definitions (1) and (2) are consistent (i.e. to see whether the θ defined in equation (1) is actually the θ that appears in the expressions for the energies), we substitute expression (2) into the trigonometric double-angle identity for tangent:

$$\tan 2\theta = \frac{2\tan\theta}{1 - \tan^2\theta} = \frac{2\left(c \pm \sqrt{c^2+1}\right)}{1 - \left(c \pm \sqrt{c^2+1}\right)^2} = \frac{2\left(c \pm \sqrt{c^2+1}\right)}{1 - \left(c^2 \pm 2c\sqrt{c^2+1} + c^2 + 1\right)}$$

$$= \frac{2\left(c \pm \sqrt{c^2+1}\right)}{-2c\left(c \pm c\sqrt{c^2+1}\right)} = \frac{-1}{c} = \frac{2\beta}{\alpha_A - \alpha_B}$$

This matches eqn (1), therefore the energies given in terms of $\tan\theta$ as defined in eqn (1) are solutions of the secular determinant.

Finally, we must solve for the coefficients in the wavefunction. The coefficients of the wavefunction can be obtained from eqns 10.36 and 10.34 (both with $S = 0$):

$$c_A = \frac{1}{\left\{1 + \left(\dfrac{\alpha_A - E_+}{\beta}\right)^2\right\}^{1/2}} = \frac{1}{\left\{1 + \left(\dfrac{-\beta\tan\theta}{\beta}\right)^2\right\}^{1/2}} = \frac{1}{(1 + \tan^2\theta)^{1/2}} = \frac{1}{\sec\theta} = \cos\theta$$

and $\quad c_B = -\left(\dfrac{\alpha_A - E_+}{\beta}\right)c_A = -\left(\dfrac{-\beta\tan\theta}{\beta}\right)\cos\theta = \sin\theta$

Thus, $\quad \psi_+ = A\cos\theta + B\sin\theta$.

For the coefficients of E_-, we will find it convenient to work with analogues of eqn 10.34 derived from the second of the secular equations (10.27b), namely

$$c_A = -\left(\frac{\alpha_B - E}{\beta}\right)c_B \quad \text{and} \quad c_B = \frac{1}{\left\{1 + \left(\dfrac{\alpha_B - E}{\beta}\right)^2\right\}^{1/2}}$$

Substituting E_- into the latter expression, we have

$$c_B = \frac{1}{\left\{1 + \left(\dfrac{\beta\tan\theta}{\beta}\right)^2\right\}^{1/2}} = \frac{1}{(1 + \tan^2\theta)^{1/2}} = \frac{1}{\sec\theta} = \cos\theta$$

and $c_A = -\left(\dfrac{\beta\tan\theta}{\beta}\right)\cos\theta = -\sin\theta$

Thus, $\psi_2 = -A\sin\theta + B\cos\theta$.

P10.24 The Roothaan equations are $\boldsymbol{FC} = \boldsymbol{Sc\varepsilon}$ or, writing the matrices explicitly,

$$\begin{pmatrix} F_{AA} & F_{AB} \\ F_{BA} & F_{BB} \end{pmatrix}\begin{pmatrix} c_{Aa} & c_{Ab} \\ c_{Ba} & c_{Bb} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\begin{pmatrix} c_{Aa} & c_{Ab} \\ c_{Ba} & c_{Bb} \end{pmatrix}\begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix}$$

Refer to eqn MB6.5 and Figure MB6.1(b) for matrix multiplication. Multiplying out the final two matrices on the right ($\boldsymbol{c\varepsilon}$) turns the equations into

$$\begin{pmatrix} F_{AA} & F_{AB} \\ F_{BA} & F_{BB} \end{pmatrix}\begin{pmatrix} c_{Aa} & c_{Ab} \\ c_{Ba} & c_{Bb} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\begin{pmatrix} \varepsilon_a c_{Aa} & \varepsilon_b c_{Ab} \\ \varepsilon_a c_{Ba} & \varepsilon_b c_{Bb} \end{pmatrix}$$

Carrying out the remaining multiplications yields four equations, one for each component of the matrices:

1,1: $F_{AA}c_{Aa} + F_{AB}c_{Ba} = \varepsilon_a c_{Aa} + S\varepsilon_a c_{Ba}$ (as shown in the main text)
1,2: $F_{AA}c_{Ab} + F_{AB}c_{Bb} = \varepsilon_b c_{Ab} + S\varepsilon_b c_{Bb}$
2,1: $F_{BA}c_{Aa} + F_{BB}c_{Ba} = S\varepsilon_a c_{Aa} + \varepsilon_a c_{Ba}$
2,2: $F_{BA}c_{Ab} + F_{BB}c_{Bb} = S\varepsilon_b c_{Ab} + \varepsilon_b c_{Bb}$

Solutions to applications

P10.26 (a) The secular determinant for cyclic H_3 is

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

Expanding the determinant yields:

$$(\alpha - E)\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} - \beta\begin{vmatrix} \beta & \beta \\ \beta & \alpha - E \end{vmatrix} + \beta\begin{vmatrix} \beta & \alpha - E \\ \beta & \beta \end{vmatrix} = 0$$

$$(\alpha - E) \times \{(\alpha - E)^2 - \beta^2\} - \beta\{\beta(\alpha - E) - \beta^2\} + \beta\{\beta^2 - (\alpha - E)\beta\} = 0$$
$$(\alpha - E)(\alpha - E - \beta)(\alpha - E + \beta) - 2\beta^2(\alpha - E - \beta) = 0$$
$$(\alpha - E - \beta)(\alpha^2 - 2\alpha E + \alpha\beta + E^2 - \beta E - 2\beta^2) = 0$$

At this point, we have a factor linear in E, from which we find a root $E = \alpha - \beta$, and a quadratic factor. One can put the quadratic factor in standard form, remembering that we are solving for E, or one can attempt to factor it further, obtaining

$$0 = (\alpha - E - \beta)(E - \alpha + \beta)(E - \alpha - 2\beta)$$

Therefore, the desired roots are $E = \boxed{\alpha - \beta \text{ (twice) and } \alpha + 2\beta}$. The energy level diagram is shown in Figure 10.10.

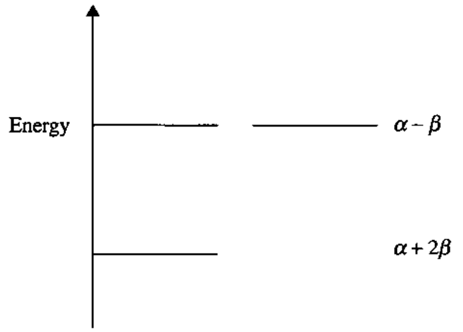


Figure 10.10

The binding energies are shown in the following table:

Species	Number of e^-	Binding energy
H_3^+	2	$2(\alpha+2\beta)=2\alpha+4\beta$
H_3	3	$2(\alpha+2\beta)+(\alpha-\beta)=3\alpha+3\beta$
H_3^-	4	$2(\alpha+2\beta)+2(\alpha-\beta)=4\alpha+2\beta$

(b) Set up the following set of chemical reactions:

$$\begin{array}{ll} H_3^+(g) \rightarrow 2\,H(g) + H^+(g) & \Delta H_1 = +849\ \text{kJ mol}^{-1} \\ H^+(g) + H_2(g) \rightarrow H_3^+(g) & \Delta H_2 = ? \\ \hline H_2(g) \rightarrow 2\,H(g) & \Delta H_3 = \{2(+217.97)-0\}\ \text{kJ mol}^{-1} \end{array}$$

$$\Delta H_2 = \Delta H_3 - \Delta H_1 = \{2(+217.97)-849\}\ \text{kJ mol}^{-1} = \boxed{-413\ \text{kJ mol}^{-1}}.$$

This is only slightly less than the binding energy of H_2 (435.94 kJ mol^{-1})

(c) $2\alpha+4\beta=-\Delta H_1=-849\ \text{kJ mol}^{-1}$

so $\beta=\dfrac{-\Delta H_1-2\alpha}{4}$, where $\Delta H_1=+849\ \text{kJ mol}^{-1}$

Species	Binding energy
H_3^+	$2\alpha+4\beta=-\Delta H_1=\boxed{-849\ \text{kJ mol}^{-1}}$
H_3	$3\alpha+3\beta=3\left(\alpha-\dfrac{\Delta H_1+2\alpha}{4}\right)=3\left(\dfrac{1}{2}\alpha-\dfrac{\Delta H_1}{4}\right)=\boxed{3(\alpha/2)-637\ \text{kJ mol}^{-1}}$
H_3^-	$4\alpha+2\beta=4\alpha-\dfrac{\Delta H_1+2\alpha}{2}=3\alpha-\dfrac{\Delta H_1}{2}=\boxed{3\alpha-425\ \text{kJ mol}^{-1}}$

As α is a negative quantity, all three of these species are expected to be stable.

P10.28 (a) The orbitals are sketched in Figure 10.11(a). ψ_1 is a bonding orbital, showing no nodes between adjacent atoms, and ψ_3 is antibonding with respect to all three atoms. ψ_2 is non-bonding, with neither constructive nor destructive interaction of the atomic orbitals of adjacent atoms.

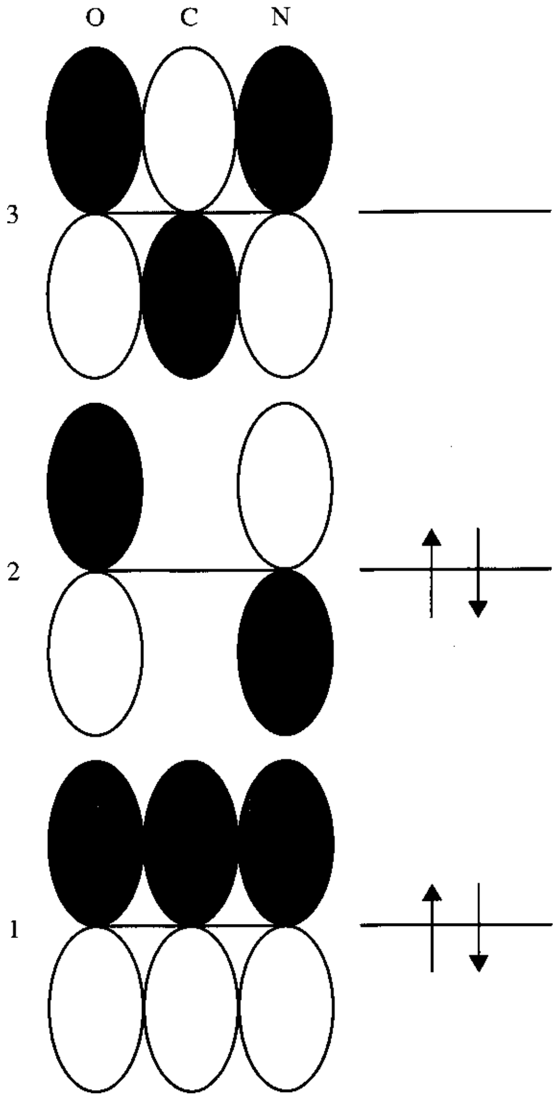
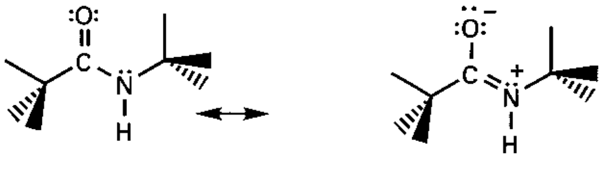


Figure 10.11(a)

(b) This arrangement only works if the entire peptide link is coplanar. For starters, the O, C, and N atoms in the peptide link must be in the same plane (call it the xy plane) if all three atoms are to contribute unhybridized p orbitals (p_z orbitals) to make the three MOs sketched above. If the peptide N and C atoms contribute p_z orbitals in the π system, then all of the σ bonds they make must be in the xy plane. Hence, the peptide O and H atoms as well as the non-peptide C atoms bound to the peptide C and N atoms must also lie in the xy plane, that is, the entire peptide linkage plus the ends of the carbon chains that they connect.



11 12

(c) The energy order of the orbitals and their occupancy are shown in Figure 10.11(a). There are four electrons to be distributed. If we look at the neutral representation of the peptide link (on the left side of the resonance structures shown here), the two electrons represented by the C=O π bond are obviously part of the π system, leaving the two lone pairs on O, the C–O σ bond, and the two other σ bonds of C as part of the σ system. Turning now to the Lewis octet of electrons around the N atom, we must assign two electrons to each of the σ bonds involving N; clearly they cannot be part of the π system. That leaves the lone pair on N, which must occupy the other orbital that N contributes to the molecule, namely the p_z orbital that is part of the π system.

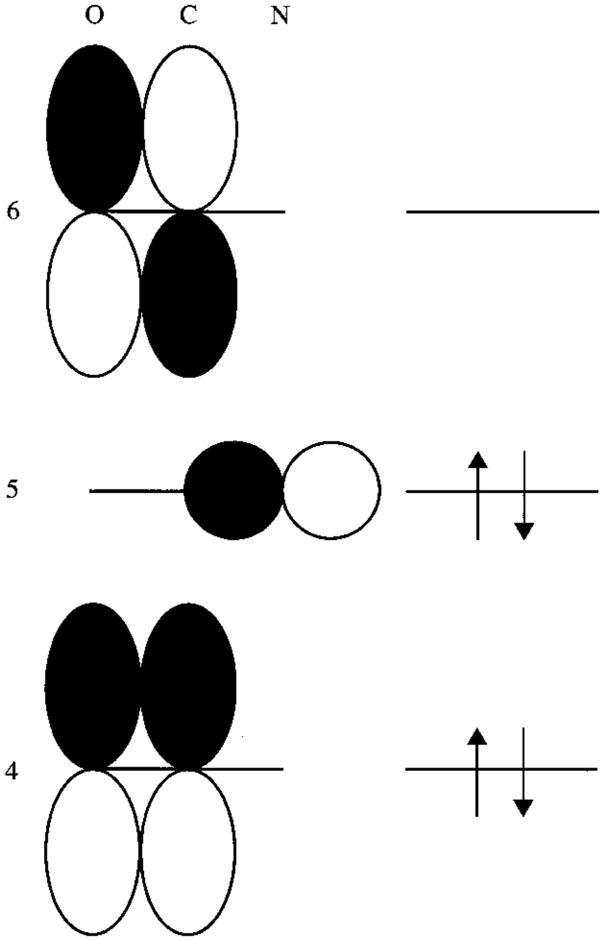


Figure 10.11(b)

(d) The orbitals of the non-planar alternative are sketched in Figure 10.11(b). ψ_4 is a bonding orbital with respect to C and O, and ψ_6 is antibonding with respect to C and O. ψ_5 is non-bonding, involving only the N atom. There are four electrons to be placed in this system, as before, two each in a bonding and non-bonding orbital.

(e) This system cannot be planar. As before, the end of the chain connected to the peptide C must be in the *xy* plane. As before, the atoms bound to N must be in a plane perpendicular to the orbital that N contributes to this system, which is itself in the *xy* plane. Only one of the N atom's σ bonds can be in both the *xy* plane and a plane perpendicular to it (because only a line can be in two perpendicular planes). Thus, the bonding partners of N other than the peptide C are forced out of the *xy* plane.

(f) The bonding MO ψ_1 must have a lower energy than the bonding MO ψ_4, for ψ_1 is bonding (stabilizing) with respect to all three atoms, while ψ_4 is bonding with respect to only two of them. Likewise, the antibonding MO ψ_3 must have a higher energy than the antibonding MO ψ_6, for ψ_3 is antibonding (destabilizing) with respect to all three atoms pairwise, while ψ_6 is antibonding only with respect to two of them. The non-bonding MOs ψ_2 and ψ_5 must have similar energies, not much different than the parameter α, for there is no significant constructive or destructive interference between adjacent atoms in either one.

(g) Because bonding orbital ψ_1 has a lower energy than ψ_4, the planar arrangement has a lower energy than the non-planar one. The total energy of the planar arrangement is

$$E_{\text{planar}} = 2E_1 + 2E_2$$

Compare this to the energy of the non-planar arrangement:

$$E_{\text{non-planar}} = 2E_4 + 2E_5 > 2E_1 + 2E_2 = E_{\text{planar}}$$

The fact that $E_3 > E_6$ is immaterial, for neither of those orbitals is occupied.

11

Molecular symmetry

Answers to discussion questions

D11.2 The point group to which a molecule belongs is determined by the symmetry elements it possesses. Therefore, the first step is to examine a model (which can be a mental picture) of the molecule for all its symmetry elements. All possible symmetry elements are described in Section 11.1. We list all that apply to the molecule of interest and then follow the assignment procedure summarized by the flow diagram in Figure 11.7 of the text.

D11.4 The permanent dipole moment is a fixed property of a molecule and as a result it must remain unchanged through any symmetry operation of the molecule. Recall that the dipole moment is a vector quantity; therefore both its magnitude and direction must be unaffected by the operation. That can only be the case if the dipole moment is coincident with *all* of the symmetry elements of the molecule. Hence, molecules belonging to point groups containing symmetry elements that do not satisfy this criterion can be eliminated. Molecules with a centre of symmetry cannot possess a dipole moment because any vector is changed through inversion. Molecules with more than one C_n axis cannot be polar since a vector cannot be coincident with more than one axis simultaneously. If the molecule has a plane of symmetry, the dipole moment must lie in the plane; if it has more than one plane of symmetry, the dipole moment must lie in the axis of intersection of these planes. A molecule can also be polar if it has one plane of symmetry and no C_n. Examination of the character tables at the end of the data section shows that the only point groups that satisfy these restrictions are C_s, C_n, and C_{nv}.

D11.6 A **representative** is a mathematical operator (usually a matrix) that represents the physical symmetry operation. The set of all these mathematical operators corresponding to all the operations of the group is called a **representation**. See Section 11.4(a) for matrix examples.

11.8 Selection rules tell us which transition probabilities between energy levels are non-zero, namely, which spectroscopic transitions will have a non-zero intensity. This occurs when at least one of the vector components of the **transition dipole moment,** $\boldsymbol{\mu}_{\mathrm{fi}}$ between the states f and i is non-zero. Each component of this vector is defined by a **transition dipole moment integral**, which we illustrate with the z component of the transition dipole moment:

$$\mu_{z,\mathrm{fi}} = -e\int \psi_{\mathrm{f}}^{*} z \psi_{\mathrm{i}}\,\mathrm{d}\tau \,[11.11]$$

where $-e$ is the charge of the electron. Group theory tells us that, if the **decomposition of the direct product** for the symmetry species of $\psi_f^* z \psi_i$ (the integrand of the transition moment integral) includes the totally symmetric representation A_1, the dipole transition moment is non-zero and, therefore, the spectroscopic transition has a non-zero probability. That is, the symmetry of the transition dipole moment integrand must either span A_1 or contain the symmetry component A_1 for an allowed transition.

D11.10 Character tables provide a way to: (a) assign symmetry symbols for orbitals, (b) know whether overlap integrals are non-zero, (c) determine what atomic orbitals can contribute to a LCAO-MO, (d) determine the maximum orbital degeneracy of a molecule, and (e) determine whether a transition is allowed.

Solutions to exercises

E11.1(b) CCl_4 belongs to the point group T_d. It has $\boxed{\text{four } C_3 \text{ axes}}$ (each C–Cl axis), $\boxed{\text{three } C_2 \text{ axes}}$ (bisecting Cl–C–Cl angles), $\boxed{\text{three } S_4 \text{ axes}}$ (the same as the C_2 axes), and $\boxed{\text{six dihedral mirror planes}}$ (each Cl–C–Cl plane). A sample of each symmetry element is shown in Figure 11.1.

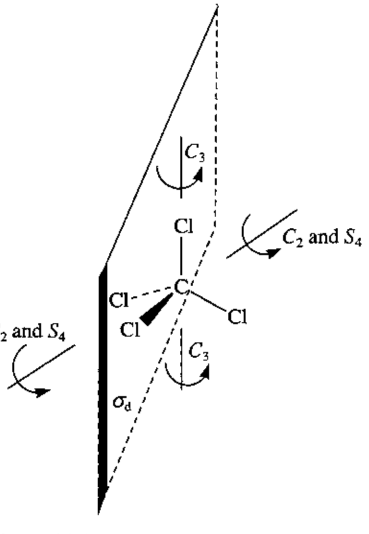


Figure 11.1

E11.2(b) See Figure 11.2.

(a) Sharpened pencil: E, C_∞, σ_v, therefore $\boxed{C_{\infty v}}$.

(b) Propellor: E, C_3, three C_2, therefore $\boxed{D_3}$.

(c) Square table: E, C_4, four σ_v, therefore $\boxed{C_{4v}}$; rectangular table: E, C_2, two σ_v, therefore $\boxed{C_{2v}}$.

(d) Person: E, σ_h (approximately), therefore $\boxed{C_s}$.

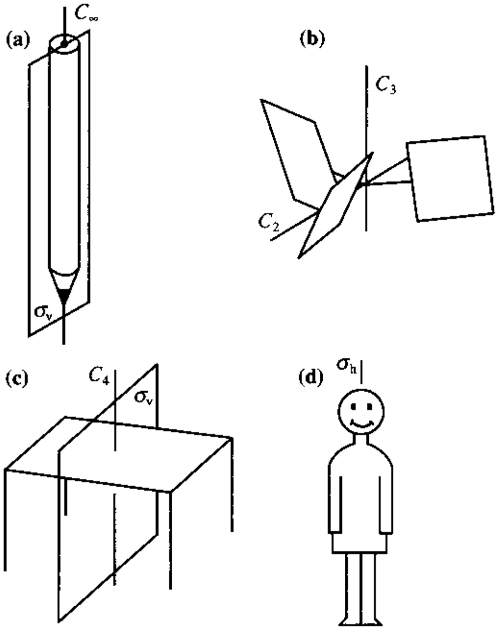


Figure 11.2

E11.3(b) We identify the symmetry elements and follow the flow chart in text Figure 11.7 to find the point group of each molecule.

(a) Naphthalene has the symmetry elements shown in Figure 11.3. There are $\boxed{\text{three } C_2}$ axes, a centre of inversion $\boxed{i}$, and $\boxed{\text{three } \sigma_h}$ mirror planes. It belongs to the point group $\boxed{D_{2h}}$.

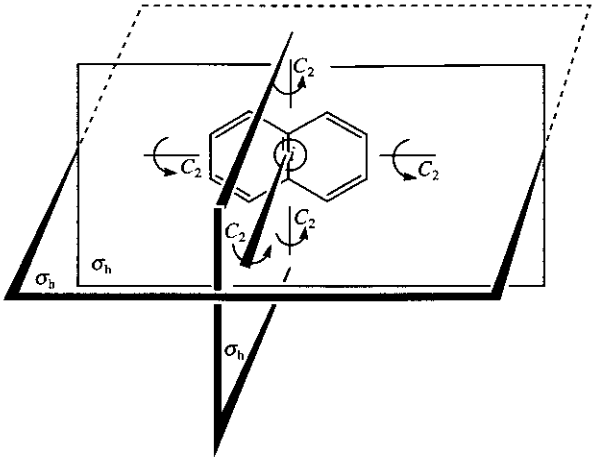


Figure 11.3

(b) Anthracene, like all linear polycyclic aromatic hydrocarbons, has a set of symmetry elements that is identical to that of naphthalene. There are $\boxed{\text{three } C_2}$ axes, a centre of inversion $\boxed{i}$, and $\boxed{\text{three } \sigma_\text{h}}$ mirror planes. It belongs to the point group $\boxed{D_{2\text{h}}}$.

(c) Dichlorobenzene isomers:

(i) 1,2-dichlorobenzene: $\boxed{E, C_2, \text{two } \sigma_\text{v}}$, $\boxed{C_{2\text{v}}}$

(ii) 1,3-dichlorobenzene: $\boxed{E, C_2, \text{two } \sigma_\text{v}}$, $\boxed{C_{2\text{v}}}$

(iii) 1,4-dichlorobenzene: $\boxed{E, \text{three } C_2, \text{three } \sigma_\text{h}, i}$, $\boxed{D_{2\text{h}}}$

E11.4(b) The following responses refer to the thought progression while proceeding through the flow chart of text Figure 11.7. Molecular structures are shown in Figure 11.4 below.

(a) HF: linear, no i, so $\boxed{C_{\infty\text{v}}}$.

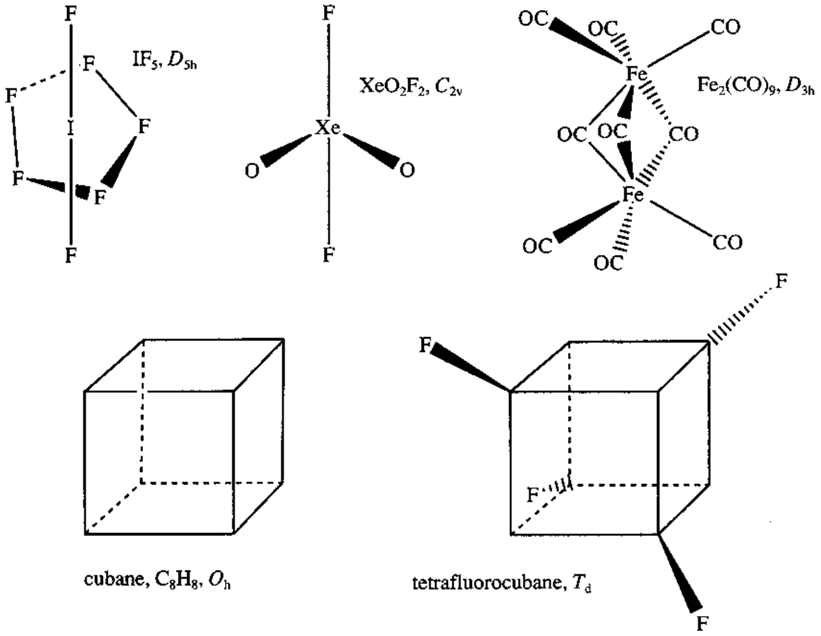
(b) IF_7: non-linear, fewer than $2C_n$ with $n > 2$, C_5, five C_2 perpendicular to C_5, σ_h, so $\boxed{\text{D}_{5\text{h}}}$.

(c) XeO_2F_2: non-linear, fewer than two C_n with $n > 2$, C_2, no C_2 perpendicular to C_2, no σ_h, two σ_v, so $\boxed{C_{2\text{v}}}$.

(d) $Fe_2(CO)_9$: non-linear, fewer than two C_n with $n > 2$, C_3, three C_2 perpendicular to C_3, σ_h, so $\boxed{D_{3\text{h}}}$.

(e) cubane (C_8H_8): non-linear, more than two C_n with $n > 2$, i, no C_5, so $\boxed{O_\text{h}}$.

(f) tetrafluorocubane: non-linear, more than two C_n with $n > 2$, no i, so $\boxed{T_\text{d}}$.



cubane, C_8H_8, O_h

tetrafluorocubane, T_d

Figure 11.4

11.5(b) Only molecules belonging to C_s, C_n, and C_{nv} groups may be polar, so:

(a) $CH_3Cl(C_{3v})$ $\boxed{\text{may be polar}}$ along the C–Cl bond

(b) $HW_2(CO)_{10}(D_{4h})$ $\boxed{\text{may not be polar}}$

(c) $SnCl_4(T_d)$ $\boxed{\text{may not be polar}}$.

E11.6(b) napthalene, D_{2h}; anthracene, D_{2h}; 1,2-dichlorobenzene, C_{2v}; 1,3-dichlorobenzene, C_{2v}; 1,4-dichlorobenzene, D_{2h}; HF, $C_{\infty v}$; IF_7, D_{5h}; XeO_2F_2, C_{2v}; $Fe_2(CO)_9$, D_{3h}; cubane, O_h; tetrafluorocubane, T_d.

A molecule cannot be chiral if it has an axis of improper rotation—including disguised or degenerate axes such as an inversion centre (S_2) or a mirror plane (S_1). In Exercises 11.3b and 11.4b, all the molecules have mirror planes, so $\boxed{\text{none}}$ can be chiral.

E11.7(b) A molecule cannot be chiral if it has an axis of improper rotation. The point group T_d has $\boxed{S_4 \text{ axes}}$ and $\boxed{\text{mirror planes } (\sigma = S_1)}$, which preclude chirality. The T_h group has, in addition, a centre of inversion ($i = S_2$).

E11.8(b) The group multiplication table of group C_{4v} is constructed by successively applying the group symmetry operations to the object shape provided in text Figure 11.8. The rotational operations are around the z-axis of the figure (i.e. the axis perpendicular to the object shape).

	E	C_4^+	C_4^-	C_2	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
E	E	C_4^+	C_4^-	C_2	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
C_4^+	C_4^+	C_2	E	C_4^-	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$
C_4^-	C_4^-	E	C_2	C_4^+	$\sigma_d(-xy)$	$\sigma(xy)$	$\sigma_v(x)$	$\sigma_v(y)$
C_2	C_2	C_4^-	C_4^+	E	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$
$\sigma_v(x)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$	$\sigma_v(y)$	E	C_2	C_4^-	C_4^+
$\sigma_v(y)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(x)$	C_2	E	C_4^+	C_4^-
$\sigma_d(xy)$	$\sigma_d(xy)$	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(-xy)$	C_4^+	C_4^-	E	C_2
$\sigma_d(-xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(xy)$	C_4^-	C_4^+	C_2	E

E11.9(b) The p_x orbital spans E_{1u} of the D_{6h} point group, while z and p_z span A_{2u}. Following the procedure discussed in Section 11.5(a), we write a table of the characters of each function and multiply the rows.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Species
p_x	2	1	−1	−2	0	0	−2	−1	1	2	0	0	E_{1u}
z	1	1	1	1	−1	−1	−1	−1	−1	−1	0	0	A_{2u}
p_z	1	1	1	1	−1	−1	−1	−1	−1	−1	0	0	A_{2u}
p_xzp_z	2	1	−1	−2	0	0	−2	−1	1	2	0	0	E_{1u}

The characters of the product p_xzp_z are those of E_{1u} alone, so the integrand does not span A_1. It follows that the $\boxed{\text{integral must be zero}}$.

E11.10(b) For a D_{6h} molecule, x and y span E_{1u} while z spans A_{2u}. Thus, the x and y components of the dipole moment [11.11] have transition integrands that span $E_{2u} \times E_{1u} \times A_{1g}$ for the $A_{1g} \rightarrow E_{2u}$ transition. By inspection of the D_{6h} character table we find the **decomposition of the direct product** to be: $E_{2u} \times E_{1u} \times A_{1g} = B_{1g} + B_{2g} + E_{1g}$. Since it does not span A_1, the x and y components of the transition integral must be zero. The transition integrand for the z component spans $E_{2u} \times A_{2u} \times A_{1g} = E_{2g}$ for the $A_{1g} \rightarrow E_{2u}$ transition. Consequently, the z component of the transition integral must also equal zero and we conclude that the transition is $\boxed{\text{forbidden}}$.

Should these considerations prove confusing, write a character table with rows that correspond to the functions of the transition integrand and multiply. Here is the table for the x and y components of the dipole moment:

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0
(x, y)	2	1	−1	−2	0	0	−2	−1	1	2	0	0
Integrand	4	−1	1	−4	0	0	4	−1	1	−4	0	0

To see whether the totally symmetric species A_{1g} is present, we form the sum over classes of the number of operations times the character of the integrand [11.8b]:

$$N(A_{1g}) = (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0$$

Since the species A_{1g} is absent, the transition is $\boxed{\text{forbidden}}$ for x- or y-polarized light. A similar analysis leads to the conclusion that A_{1g} is absent from the product $A_{1g}E_{2u}z$, therefore the transition is forbidden.

E11.11(b) We first determine how x, y, and z individually transform under the operations of the D_2 group. Using these results we determine how the product xyz transforms, from which we extract the symmetry character χ.

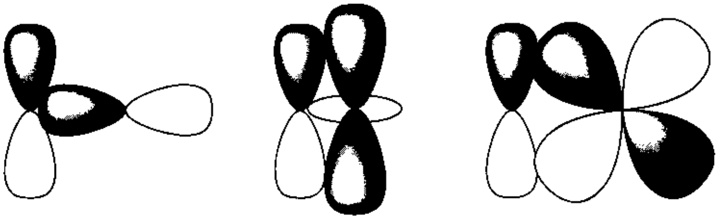
Under each operation the functions transform as follows:

	E	C_2^x	C_2^y	C_2^z
x	x	x	$-x$	$-x$
y	y	$-y$	y	$-y$
z	z	$-z$	$-z$	z
xyz	xyz	xyz	xyz	xyz
χ	1	1	1	1

From the D_2 character table, we see that this set of χ characters belongs to the totally symmetric A_1 species.

E11.12(b) NO_3^- and SO_3 both belong to the D_{3h} group. It is often helpful to visualize the possible bonding patterns, so before using the D_{3h} character table we first use our knowledge of the wavefunction behavior in the view of simple molecular orbital theory.

With three O atoms providing valence p_z orbitals (perpendicular to the molecular plane) in the combination $2p_z(A) - p_z(B) - p_z(C)$ only π bonding is possible with the N atom. This means that $\boxed{\text{only the valence } p_z \text{ orbital of N}}$ can have a non-zero overlap with this O combination. Furthermore, $\boxed{\text{only the } p_z\text{, the } d_{xz} \text{ and the } d_{yz} \text{ orbitals of S}}$ have non-zero overlap in this π system. To see this, look for non-zero overlap between Op_z and Np_x orbitals in Figure 11.5(a). (The orbital has a positive wavefunction sign in shaded lobes and a negative wavefunction sign in unshaded lobes.) Clearly, the overlap of positive lobes (constructive interference) is exactly cancelled by the overlap of a negative lobe with a positive lobe (destructive interference) to give a net zero overlap. The same thing happens with the p_z/d_{z^2}, overlap shown in Figure 11.5(b). The p_z/d_{xz} overlap shown in Figure 11.5(c) yields a net non-zero overlap because both the overlap of positive lobes and the overlap of negative lobes results in constructive interference.



(a) p_z/p_x overlap (b) p_z/d_{z^2} overlap (c) p_z/d_{xz} overlap

Figure 11.5

The D_{3h} character table provides the same solution. To see this, we must find the irreducible representations (symmetry species) spanned by the oxygen p_z orbitals. The nitrogen orbital must belong to one of these representations to achieve a non-zero overlap because the totally symmetric overlap integrand is only achieved when an irreducible representation is multiplied by itself (Section 11.5(a)).

To find the symmetry species spanned by the oxygen p_z orbitals, we use a quick rule for determining the character of the basis function under each symmetry operation of the group: count 1 each time a basis function is left unchanged by the operation because only these functions give a non-zero entry on the diagonal of the matrix representative. In some cases there is a sign change, $(\ldots -f \ldots) \leftarrow (\ldots f \ldots)$; then −1 occurs on the diagonal, and so count −1. The character of the identity is always equal to the dimension of the basis since each function contributes 1 to the trace. Figure 11.6 is used to evaluate the effect of the operations on the oxygen p_z orbitals of $2p_z(A) - p_z(B) - p_z(C)$.

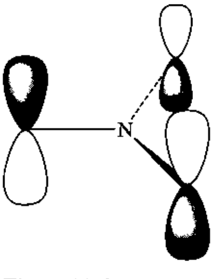


Figure 11.6

E: All three orbitals are left unchanged, hence $\chi = 3$
σ_h: Sign changes on all three orbitals, hence $\chi = -3$
C_3: No orbital is left unchanged, hence $\chi = 0$
S_3: No orbital is left unchanged, hence $\chi = 0$
C_2': Sign changes on one orbital, hence $\chi = -1$
σ_v: One orbital is left unchanged, hence $\chi = 1$

Here is a tabulated summary of the characters:

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
$2p_z(A) - p_z(B) - p_z(C)$	3	−3	0	0	−1	1

Inspection of the D_{3h} character table reveals that the oxygen p_z orbitals span $A_2'' + E''$ because the sum of their characters yields those of the table. Further inspection of the D_{3h} character table reveals that z belongs to A_2'' and both xz and yz belong to E''. Consequently, only p_z, d_{xz}, and d_{yz} orbitals of the central atom have non-zero overlap with the oxygen combination. This is exactly what is expected.

E11.13(b) The product $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$ must contain A_1 (Section 11.6). Then, since $\Gamma_i = B_1$, $\Gamma(\mu) = \Gamma(y) = B_2$ (C_{2v} character table), we can draw up the following table of characters.

	E	C_2	σ_v	σ_v'	
B_2	1	−1	−1	1	
B_1	1	−1	1	−1	
$B_1 \times B_2$	1	1	−1	−1	$= A_2$

Hence, the upper state is $\boxed{A_2}$, because $A_2 \times A_2 = A_1$.

E11.14(b)

$D_2, h = 4$	E	C_2^z	C_2^y	C_2^x
A_1	1	1	1	1
B_1	1	1	−1	−1
B_2	1	−1	1	−1
B_3	1	−1	−1	1

$$N_n = \frac{1}{h}\sum_R \chi^{(n)}(R)\chi(R) \quad [11.8b], \quad \text{where } \chi(R) = (6, -2, 0, 0)$$

$$N_{A_1} = \tfrac{1}{4}\{1(1 \times 6) + 1(1 \times (-2)) + 1(1 \times 0) + 1(1 \times 0)\} = 1$$

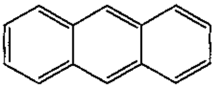
$$N_{B_1} = \tfrac{1}{4}\{1(1 \times 6) + 1(1 \times (-2)) + 1(-1 \times 0) + 1(-1 \times 0)\} = 1$$

$$N_{B_2} = \tfrac{1}{4}\{1(1 \times 6) + 1(-1 \times (-2)) + 1(1 \times 0) + 1(-1 \times 0)\} = 2$$

$$N_{B_3} = \tfrac{1}{4}\{1(1 \times 6) + 1(-1 \times (-2)) + 1(-1 \times 0) + 1(1 \times 0)\} = 2$$

Thus, this set of basis functions spans $\boxed{A_1 + B_1 + 2B_2 + 2B_3}$.

E11.15(b) (a) Anthracene belongs to the D_{2h} point group.



The components of μ span $B_{3u}(x)$, $B_{2u}(y)$, and $B_{1u}(z)$. The totally symmetric ground state is A_g. Since $A_g \times \Gamma = \Gamma$ in this group, the accessible upper terms are $\boxed{B_{3u}}$ (x-polarized), $\boxed{B_{2u}}$ (y-polarized), and $\boxed{B_{1u}}$ (z-polarized).

(b) Coronene, like benzene, belongs to the D_{6h} group. The integrand of the transition dipole moment must be or contain the A_{1g} symmetry species. That integrand for transitions from the ground state is $A_{1g}qf$, where q is x, y, or z and f is the symmetry species of the upper state. Since the ground state is already totally symmetric, the product qf must also have A_{1g} symmetry for the entire integrand to have A_{1g} symmetry. Since the different symmetry species are orthogonal, the only way qf can have A_{1g} symmetry is if q and f have the same symmetry. Such combinations include zA_{2u}, xE_{1u}, and yE_{1u}, therefore we conclude that transitions are allowed to states with $\boxed{A_{2u} \text{ or } E_{1u}}$ symmetry.

E11.16(b) Consider the integral $I = \int_{-a}^{a} z(3z^2 - 1)\mathrm{d}x = 3\int_{-a}^{a} z^3\mathrm{d}x - \int_{-a}^{a} z\mathrm{d}z = 3I_2 - I_1$. (We have used z as the dummy variable in the integration because the σ_h plane inverts this axis in the C_s group.) z spans A″ of the C_s group. Consequently, I_1 is necessarily zero because it does not span the totally symmetric species A′. The integrand of I_2 is the product $z \times z \times z$, which spans $A'' \times A'' \times A'' = A' \times A'' = A''$. Consequently, I_2 is also necessarily zero and we conclude that integral I is necessarily zero.

Solutions to problems

Solutions to numerical problems

P11.2 The operations for construction of the C_{2h} group multiplication table are illustrated in Figure 11.7. Note that $R^2 = E$ for all the operations of this group, that $ER = RE = R$, and that $RS = SR$. Since $C_2\sigma_h = i$, $\sigma_h i = C_2$, and $iC_2 = \sigma_h$ we can draw up the following group multiplication table:

	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

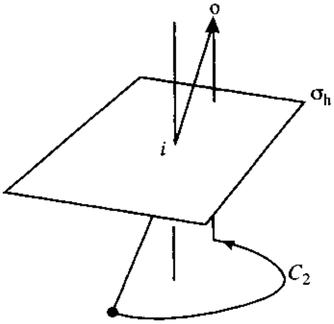


Figure 11.7

The $\boxed{\textit{trans}\text{-CHCl=CHCl}}$ molecule belongs to the group C_{2h}.

P11.4 Refer to Figure 11.3 of the text. Place orbitals h_1 and h_2 on the H atoms and s, p_x, p_y, and p_z on the O atom. The z-axis is the C_2 axis; x lies perpendicular to σ_v', y lies perpendicular to σ_v. Then, draw up the following table of the effect of the operations on the basis:

	E	C_2	σ_v	σ_v'
h_1	h_1	h_2	h_2	h_1
h_2	h_2	h_1	h_1	h_2
s	s	s	s	s
p_x	p_x	$-p_x$	p_x	$-p_x$
p_y	p_y	$-p_y$	$-p_y$	p_y
p_z	p_z	p_z	p_z	p_z

Express the columns headed by each operations R in the form

(new) ← (original)$D(R)$

where $D(R)$ is the 6×6 representative of the operation R. We use the methods set out in Section 11.4(a).

(i) E: $(h_1, h_2, s, p_x, p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by the 6×6 unit matrix.

(ii) C_2: $(h_2, h_1, s, -p_x, -p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$\boldsymbol{D}(C_2) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

(iii) σ_v: $(h_2, h_1, s, p_x, -p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$\boldsymbol{D}(\sigma_v) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

(iv) σ_v': $(h_1, h_2, s, -p_x, p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$\boldsymbol{D}(\sigma_v') = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

(a) To confirm the correct representation of $C_2\sigma_v = \sigma_v'$, we write

$$\boldsymbol{D}(C_2)\boldsymbol{D}(\sigma_v) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \boldsymbol{D}(\sigma_v')$$

(b) Similarly, to confirm the correct representation of $\sigma_v\sigma_v' = C_2$, we write

$$\boldsymbol{D}(\sigma_v)\boldsymbol{D}(\sigma_v') = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \boldsymbol{D}(C_2)$$

(a) The characters of the representatives are the sums of their diagonal elements:

E	C_2	σ_v	σ_v'
6	0	2	4

(b) The characters are not those of any one irreducible representation, so the representation is reducible.

(c) The sum of the characters of the specified sum is

	E	C_2	σ_v	σ_v'
$3A_1$	3	3	3	3
B_1	1	−1	1	−1
$2B_2$	2	−2	−2	2
$3A_1 + B_1 + 2B_2$	6	0	2	4

which is the same as the original. Therefore, the representation is $3A_1 + B_1 + 2B_2$.

P11.6 Representation 1: $\boldsymbol{D}(C_3)\boldsymbol{D}(C_2) = 1 \times 1 = 1 = \boldsymbol{D}(C_6)$

and from the C_{6v} character table this is either A_1 or A_2. Hence, either $\boldsymbol{D}(\sigma_v) = \boldsymbol{D}(\sigma_d) = \boxed{+1 \text{ or } -1}$, respectively.

Representation 2: $\boldsymbol{D}(C_3)\boldsymbol{D}(C_2) = 1 \times (-1) = -1 = \boldsymbol{D}(C_6)$

and from the C_{6v} character table this is either B_1 or B_2. Hence, either

$\boldsymbol{D}(\sigma_v) = -\boldsymbol{D}(\sigma_d) = \boxed{1}$ or $\boldsymbol{D}(\sigma_v) = -\boldsymbol{D}(\sigma_d) = \boxed{-1}$, respectively.

P11.8 A quick rule for determining the character without first having to set up the matrix representation is to count 1 each time a basis function is left unchanged by the operation, because only these functions give a non-zero entry on the diagonal of the matrix representative. In some cases there is a sign change, $(\ldots -f \ldots) \leftarrow (\ldots f \ldots)$, then -1 occurs on the diagonal, and so count -1. The character of the identity is always equal to the dimension of the basis since each function contributes 1 to the trace.

E: All four orbitals are left unchanged, hence $\chi = 4$

C_3: One orbital is left unchanged, hence $\chi = 1$

C_2: No orbitals are left unchanged, hence $\chi = 0$

σ_d: Two orbitals are left unchanged, hence $\chi = 2$

S_4: No orbitals are left unchanged, hence $\chi = 0$

The character set [4, 1, 0, 2, 0] spans $\boxed{A_1 + T_2}$. Inspection of the character table of the group T_d shows that an s orbital spans A_1 and that the three p orbitals on the C atom span T_2. Hence, the $\boxed{\text{s and p}}$ orbitals of the C atom may form molecular orbitals with the four H1s orbitals. In T_d, the d orbitals of the central atom span $E + T_2$ (character table, final column), and so only the T_2 set $\boxed{(d_{xy}, d_{yz}, d_{zx})}$ may contribute to molecular orbital formation with the H orbitals.

P11.10 The most distinctive symmetry operation is the $\boxed{S_4}$-axis through the central atom and aromatic nitrogens on both ligands. That axis is also a $\boxed{C_2}$-axis. The group is $\boxed{S_4}$.

P11.12 (a) Working through the flow diagram (Figure 11.7) in the text, we note that there are no C_n-axes with $n > 2$ (for the C_3-axes present in a tetrahedron are not symmetry axes any longer), but it does have C_2-axes; in fact it has $2C_2$-axes perpendicular to whichever C_2 we call principal: it has no σ_h, but it has $2\sigma_d$. So the point group is $\boxed{D_{2d}}$.

(b) Within this point group, the distortion belongs to the fully symmetric species $\boxed{A_1}$ for its motion is unchanged by the S_4 operation, either class of C_2, or σ_d.

(c) The resulting structure is a square bipyramid, but with one pyramid's apex farther from the base than the other's. Working through the flow diagram in Figure 11.7, we note that there is only one C_n-axis with $n > 2$, namely a C_4-axis; it has no C_2-axes perpendicular to the C_4, and it has no σ_h, but it has $4\sigma_v$. So the point group is $\boxed{C_{4v}}$.

(d) Within this point group, the distortion belongs to the fully symmetric species $\boxed{A_1}$. The translation of atoms along the given axis is unchanged by any symmetry operation for the motion is contained within each of the group's symmetry elements.

11.14 (a) xyz changes sign under the inversion operation (one of the symmetry elements of a cube), hence it does not span A_{1g} and its integral $\boxed{\text{must be zero}}$.

(b) xyz spans A_1 in T_d [Problem 11.13] and so its integral $\boxed{\text{need not be zero}}$.

(c) $xyz \rightarrow -xyz$ under $z \rightarrow -z$ (the σ_h operation in D_{6h}), and so its integral $\boxed{\text{must be zero}}$.

11.16 We shall adapt the simpler subgroup C_{6v} of the full D_{6h} point group. The six p_z orbitals span $A_1 + B_1 + E_1 + E_2$, and are

$$a_1 = \frac{1}{\sqrt{6}}(p_{z1} + p_{z2} + p_{z3} + p_{z4} + p_{z5} + p_{z6})$$

$$b_1 = \frac{1}{\sqrt{6}}(p_{z1} - p_{z2} + p_{z3} - p_{z4} + p_{z5} - p_{z6})$$

$$e_2 = \begin{cases} \dfrac{1}{\sqrt{12}}(2p_{z1} - p_{z2} - p_{z3} + 2p_{z4} - p_{z5} - p_{z6}) \\ \frac{1}{2}(p_{z2} - p_{z3} + p_{z5} - p_{z6}) \end{cases}$$

$$e_1 = \begin{cases} \dfrac{1}{\sqrt{12}}(2p_{z1} + p_{z2} - p_{z3} - 2p_{z4} - p_{z5} + p_{z6}) \\ \frac{1}{2}(p_{z2} + p_{z3} - p_{z5} - p_{z6}) \end{cases}$$

The Hamiltonian transforms as A_1, therefore all integrals of the form $\int \psi' H \psi \, d\tau$ vanish unless ψ' and ψ belong to the same symmetry species. It follows that the secular determinant factorizes into four determinants:

$$A_1: \quad H_{a_1a_1} = \tfrac{1}{6}\int (p_{z1} + \cdots + p_{z6}) H (p_{z1} + \cdots + p_{z6}) d\tau = \alpha + 2\beta$$

$$B_1: \quad H_{b_1b_1} = \tfrac{1}{6}\int (p_{z1} - p_{z2} + \cdots) H (p_{z1} - p_{z2} + \cdots) d\tau = \alpha - 2\beta$$

$$E_2: \quad H_{e_2(a)e_2(a)} = \alpha - \beta, \; H_{e_2(b)e_2(b)} = \alpha - \beta, \; H_{e_2(a)e_2(b)} = 0$$

Hence, $\begin{vmatrix} \alpha - \beta - \varepsilon & 0 \\ 0 & \alpha - \beta - \varepsilon \end{vmatrix} = 0$ solves to $\varepsilon = \alpha - \beta$ (twice)

$$E_1: \quad H_{e_1(a)e_1(a)} = \alpha + \beta, \; H_{e_1(b)e_1(b)} = \alpha + \beta, \; H_{e_1(a)e_1(b)} = 0$$

Hence, $\begin{vmatrix} \alpha + \beta - \varepsilon & 0 \\ 0 & \alpha + \beta - \varepsilon \end{vmatrix} = 0$ solves to $\varepsilon = \alpha + \beta$ (twice)

P11.18 (a) For a photon to induce a spectroscopic transition, the transition moment (μ) must be non-zero. The transition moment is the integral $\int \psi_f^* \mu \psi_i \, d\tau$, where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation of the molecule's point group. We can answer the first part of the question without reference to the character table, by considering the character of the integrand under inversion. Each component of μ has u character, but each state has g character; the integrand is g × g × u = u, so the integral vanishes and the $\boxed{\text{transition is not allowed}}$.

(b) However, if a vibration breaks the inversion symmetry, a look at the *I* character table shows that the components of μ have T_1 character. To find the character of the integrand, we multiply together the characters of its factors. For the transition to T_1:

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_1	1	1	1	1	1
$\mu(T_1)$	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	-1
T_1	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	-1
Integrand	9	$\frac{1}{2}(3+\sqrt{5})$	$\frac{1}{2}(3-\sqrt{5})$	0	1

The decomposition of the characters of the integrand into those of the irreducible representations is difficult to do by inspection, but when accomplished it is seen to contain A_1, therefore the transition to T_1 would become allowed. It is easier to use eqn 11.8b to determine the coefficient of A_1 in the integrand:

$$N_{A_1} = \frac{1}{h}\sum_R \chi^{(A_1)}(R)\chi(R) = \{9 + 12[\tfrac{1}{2}(3+\sqrt{5})] + 12[\tfrac{1}{2}(3-\sqrt{5})] + 20(0) + 15(1)\}/60 = 1$$

So, the integrand contains A_1, and the $\boxed{\text{transition to } T_1 \text{ would become allowed}}$.

For the transition to G:

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_1	1	1	1	1	1
$\mu(T_1)$	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	-1
G	4	-1	-1	1	0
Integrand	12	$-\frac{1}{2}(1+\sqrt{5})$	$-\frac{1}{2}(1-\sqrt{5})$	0	0

Eqn 11.8b, the little orthogonality theorem, gives the coefficient of A_1 in the integrand as

$$N_{A_1} = \frac{1}{h}\sum_R \chi^{(A_1)}(R)\chi(R) = \{12 + 12[-\tfrac{1}{2}(1+\sqrt{5})] + 12[-\tfrac{1}{2}(1-\sqrt{5})] + 20(0) + 15(0)\}/60 = 0$$

So, the integrand does not contain A_1, and the $\boxed{\text{transition to G would still be forbidden}}$.

Solutions to applications: astrophysics and biology

P11.20 The shape of this molecule is shown in Figure 11.8.

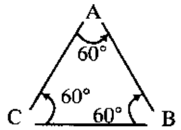


Figure 11.8

(a) Symmetry elements $\boxed{E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v}$

Point group $\boxed{D_{3h}}$

(b) $$\boldsymbol{D}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \boldsymbol{D}(\sigma_h)$$

$$\boldsymbol{D}(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \boldsymbol{D}(C_3') = \boldsymbol{D}^2(C_3) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\boldsymbol{D}(S_3) = \boldsymbol{D}(C_3), \quad \boldsymbol{D}(S_3') = \boldsymbol{D}^2(S_3) = \boldsymbol{D}(C_3')$$

C_3' and S_3' are counter clockwise rotations.
σ_v is through A and perpendicular to B–C.
σ_v' is through B and perpendicular to A–C.
σ_v'' is through C and perpendicular to A–B.

$$\boldsymbol{D}(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \boldsymbol{D}(\sigma_v') = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \boldsymbol{D}(\sigma_v'') = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\boldsymbol{D}(C_2) = \boldsymbol{D}(\sigma_v), \quad \boldsymbol{D}(C_2') = \boldsymbol{D}(\sigma_v'), \quad \boldsymbol{D}(C_2'') = \boldsymbol{D}(\sigma_v''),$$

(c) Example of elements of group multiplication table

$$\boldsymbol{D}(C_3)\boldsymbol{D}(C_2) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \boldsymbol{D}(\sigma_v'')$$

$$\boldsymbol{D}(\sigma_v')\boldsymbol{D}(\sigma_v) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} = \boldsymbol{D}(C_3')$$

D_{3h}	E	C_3	C_2	σ_v	σ_v'	σ_h	…
E	E	C_3	C_2	σ_v	σ_v'	σ_h	…
C_3	C_3	C_3'	σ_v''	σ_v''	σ_v	C_3	…
C_2	C_2	σ_v'	E	E	C_3	C_2	…
σ_v	σ_v	σ_v'	E	E	C_3	σ_v	…
σ_v'	σ_v'	σ_v''	C_3	C_3'	E	σ_v'	…
σ_h	σ_h	C_3	C_2	σ_v	σ_v'	E	…
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋱

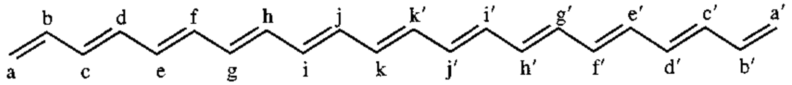
(d) First, determine the number of s orbitals (the basis has three s orbitals) that have unchanged positions after application of each symmetry species of the D_{3h} point group.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Unchanged basis members	3	0	1	3	0	1

This is not one of the irreducible representations reported in the D_{3h} character table but inspection shows that it is identical to $A_1' + E'$. This allows us to conclude that the three s orbitals span $\boxed{A_1' + E'}$.

COMMENT. The multiplication table in part (c) is not strictly speaking *the* group multiplication; it is instead the multiplication table for the matrix representations of the group in the basis under consideration.

P11.22 (a) Following the flow chart in Figure 11.7 of the text, note that the molecule is not linear (at least not in the mathematical sense); there is only one C_n axis (a C_2), and there is a σ_h. The point group, then, is $\boxed{C_{2h}}$.



(b) The $2p_z$ orbitals are transformed under the symmetry operations of the C_{2h} group as follows.

	a	a′	b	b′	c	c′	…	j	j′	k	k′	χ
E	a	a′	b	b′	c	c′	…	j	j′	k	k′	22
C_2	a′	a	b′	b	c′	c	…	j′	j	k′	k	0
i	–a′	–a	–b′	–b	–c′	–c	…	–j′	–j	–k′	–k	0
σ_h	–a	–a′	–b	–b′	–c	–c′	…	–j	–j′	–k	–k′	–22

To find the irreducible representations that these orbitals span, we multiply the characters of orbitals by the characters of the irreducible representations, sum those products, and divide the sum by the order h of the group (as in Section 11.5(a)). The table below illustrates the procedure, beginning at left with the C_{2h} character table.

	E	C_2	i	σ_h	Product	E	C_2	i	σ_h	Sum/h
A_g	1	1	1	1		22	0	0	–22	0
A_u	1	1	–1	–1		22	0	0	22	11
B_g	1	–1	1	–1		22	0	0	22	11
B_u	1	–1	–1	1		22	0	0	–22	0

The orbitals span $\boxed{11A_u + 11B_g}$.

To find symmetry-adapted linear combinations (SALCs), follow the procedure described in Section 11.5(c). Refer to the table above that displays the transformations of the original basis orbitals. To find SALCs of a given symmetry species, take a column of the table, multiply each entry by the character of the species' irreducible representation, sum the terms in the column, and divide by the order of the group. For example, the characters of species A_u are [1, 1, 1, 1], so the columns to be summed are identical to the columns in the table above. Each column sums to zero, so we conclude that there are no SALCs of A_g symmetry. (No surprise: the orbitals span only A_u and B_g). An A_u SALC is obtained by multiplying the characters 1, 1, –1, –1 by the first column: $\frac{1}{4}(a + a' + a' + a) = \frac{1}{2}(a + a')$.

The A_u combination from the second column is the same. There are 11 distinct A_u combinations in all: $\boxed{\tfrac{1}{2}(a + a'), \tfrac{1}{2}(b + b'), \ldots \tfrac{1}{2}(k + k')}$

The B_g combination from the first column is: $\tfrac{1}{4}(a - a' - a' + a) = \tfrac{1}{2}(a - a')$.

The B_g combination from the second column is the same. There are 11 distinct B_g combinations in all: $\boxed{\tfrac{1}{2}(a - a'), \tfrac{1}{2}(b - b'), \ldots \tfrac{1}{2}(k - k')}$. There are no B_u combinations, as the columns sum to zero.

(c) The structure is labelled to match the row and column numbers shown in the determinant. The Hückel secular determinant is:

$$\begin{array}{c|cccccccccccccc|}
 & \mathrm{a} & \mathrm{b} & \mathrm{c} & \ldots & \mathrm{i} & \mathrm{j} & \mathrm{k} & \mathrm{k}' & \mathrm{j}' & \mathrm{i}' & \ldots & \mathrm{c}' & \mathrm{b}' & \mathrm{a}' \\
\mathrm{a} & \alpha-E & \beta & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{b} & \beta & \alpha-E & \beta & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{c} & 0 & \beta & \alpha-E & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
\mathrm{i} & 0 & 0 & 0 & \ldots & \alpha-E & \beta & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{j} & 0 & 0 & 0 & \ldots & \beta & \alpha-E & \beta & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{k} & 0 & 0 & 0 & \ldots & 0 & \beta & \alpha-E & \beta & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{k}' & 0 & 0 & 0 & \ldots & 0 & 0 & \beta & \alpha-E & \beta & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{j}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & \beta & \alpha-E & \beta & \ldots & 0 & 0 & 0 \\
\mathrm{i}' & 0 & 0 & 0 & \ldots & 0 & 0 & & 0 & 0 & \beta & \alpha-E & 0 & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
\mathrm{c}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & \alpha-E & \beta & 0 \\
\mathrm{b}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & \beta & \alpha-E & \beta \\
\mathrm{a}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & \beta & \alpha-E
\end{array}$$

The energies of the filled orbitals are $\alpha + 1.98137\beta$, $\alpha + 1.92583\beta$, $\alpha + 1.83442\beta$, $\alpha + 1.70884\beta$, $\alpha + 1.55142\beta$, $\alpha + 1.36511\beta$, $\alpha + 1.15336\beta$, $\alpha + 0.92013\beta$, $\alpha + 0.66976\beta$, $\alpha + 0.40691\beta$, and $\alpha + 0.13648\beta$. The π energy is 27.30729β.

(d) The ground state of the molecule has A_g symmetry by virtue of the fact that its wavefunction is the product of doubly occupied orbitals, and the product of any two orbitals of the same symmetry has A_g character. If a transition is to be allowed, the transition dipole must be non-zero, which in turn can only happen if the representation of the product $\Psi_f^* \mu \Psi_i$ includes the totally symmetric species A_g. Consider first transitions to another A_g wavefunction, in which case we need the product $A_g \times \mu \times A_g$. Now $A_g \times A_g = A_g$, and the only character that returns A_g when multiplied by A_g is A_g itself. No component of the dipole operator belongs to species A_g, so no $A_g \leftarrow A_g$ transitions are allowed. (**Note:** Such transitions are transitions from an orbital occupied in the ground state to an excited-state orbital of the same symmetry.) The other possibility is a transition from an orbital of one symmetry (A_u or B_g) to the other; in that case, the excited-state wavefunction will have symmetry of $A_u \times B_g = B_u$ from the two singly occupied orbitals in the excited state. The symmetry of the transition dipole, then, is $A_g \times \mu \times B_u = \mu \times B_u$, and the only species that yields A_g when multiplied by B_u is B_u itself. The x and y components of the dipole operator belongs to species B_u, so these transitions are allowed.

12

Molecular spectroscopy 1: rotational and vibrational spectra

Answers to discussion questions

D12.2 The gross selection rules tell us which are the allowed spectroscopic transitions. For both microwave and infrared spectroscopy, the allowed transitions depend on the existence of an oscillating dipole moment that can stir the electromagnetic field into oscillation (and vice versa for absorption). For microwave rotational spectroscopy, this implies that the molecule must have a permanent dipole moment, which is equivalent to an oscillating dipole when the molecule is rotating. See Figure 12.14 of the text. In the case of infrared vibrational spectroscopy, the physical basis of the gross selection rule is that the molecules have a structure that allows for the existence of an oscillating dipole moment when the molecule vibrates. Polar molecules necessarily satisfy this requirement, but non-polar molecules may also have a fluctuating dipole moment on vibration. See Figure 12.25.

D12.4 See Section 12.7, and in particular *Justification* 12.1, for a thorough discussion of the principles that govern the influence of nuclear spin and nuclear statistics on the appearance of molecular spectra. Here, we will only summarize the basic principles involved and illustrate the effect on the rotational spectra of molecules with a couple of examples. Nuclear spin determines the selective occupation of molecular rotational states that stems from the requirement of the Pauli principle and the presence of identical nuclei. If the rotation of a molecule results in the interchange of identical nuclei, the wavefunction must change in accord with the Pauli principle (stay the same for bosons; change sign for fermions). Hence, certain rotational states are forbidden. In the case where the interchanged nuclei are bosons, this restriction eliminates occupation of states with J odd. So for CO_2 where the interchanged O nuclei are bosons of spin 0, only even values of J are permissible. Consequently, in the Raman spectrum of CO_2 only alternate lines appear. For molecular hydrogen and fluorine both with nuclei of spin $\frac{1}{2}$ fermions, the situation is more complicated, as explained in *Justification* 12.1. The population of the odd J and even J states is in the ratio of 3:1, as given by eqn 12.26, hence the intensities of transitions originating in these levels will be in the ratio of 3:1. See Figure 12.20 of the text for an illustration of the effect of nuclear spin on the appearance of the rotational Raman spectra of these molecules.

D12.6 Isotopic substitution can change the spin of the nuclei in the molecule, and as explained in the answer to Discussion question 12.4 above, the appearance of the rotational spectra of molecules is determined by the nuclear spin of the atoms in the molecule. Hence, in general we expect that isotopic substitution will change rotational spectra. Vibrational frequencies are determined by the effective masses of the group of atoms participating in the mode of vibration. Since isotopes have different masses, isotopic substitution changes the effective mass of the molecule, hence, in general, the vibrational frequencies are changed and the vibrational spectrum will be (slightly) different. Not all vibrational frequencies are necessarily changed by isotopic substitution, however. For example, since the mass of ^{13}C is greater than the mass of ^{12}C, in general we expect that vibrational frequencies would be slightly different in $^{13}CO_2$ than in $^{12}CO_2$. However, in the symmetric stretch of CO_2, the C atom is stationary, and the effective mass of the mode depends only on the O atoms. Consequently, we expect that the vibrational frequency of this mode would be independent of the mass of the carbon atom.

Solutions to exercises

E12.1(b) Polar molecules show a pure rotational absorption spectrum, therefore select the polar molecules based on their well-known structures. Alternatively, determine the point groups of the molecules and use the rule that only molecules belonging to C_n, C_{nv}, and C_s may be polar, and in the case of C_n and C_{nv} that dipole must lie along the rotation axis. Hence, all are polar molecules.

Their point group symmetries are

(a) H_2O, C_{2v}, (b) H_2O_2, C_2, (c) NH_2, C_{3v}, (d) N_2O, $C_{\infty v}$

$\boxed{\text{All}}$ show a pure rotational spectrum.

E12.2(b) A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property, so $\boxed{CH_2Cl_2}$, $\boxed{CH_3CH_3}$, and $\boxed{N_2O}$ can display rotational Raman spectra; SF_6 cannot.

E12.3(b) Si^1H_4 is a tetrahedral molecule, hence its moment of inertia is given by

$$I = \tfrac{8}{3} m_A R^2 \,[\text{Table 12.1}] = \tfrac{8}{3} \times 1.0078 \times 1.66054 \times 10^{-27}\,\text{kg} \times R^2$$

The distance $R(\text{Si-}^1\text{H})$ is given as 147.98 pm. The above formula then yields

$$\boxed{I = 9.772 \times 10^{-47}\,\text{kg m}^2}$$

The moment of inertia of Si^2H_4 is given by the same formula. We assume R remains unchanged by the isotopic substitution, but the mass is different. The moment of inertia changes by the factor

$$\frac{m_{^2\text{H}}}{m_{^1\text{H}}} = \frac{2.0140\, m_u}{1.0078\, m_u} = \boxed{1.9984}$$

E12.4(b) $H^{12}C^{35}Cl_3$ is a symmetric rotor; its moments of inertia are given by the formulas [Table 12.1]

$$I_{\parallel} = 2m_{Cl}(1 - \cos\theta)R^2 \quad \text{and}$$

$$I_{\perp} = m_{Cl}(1 - \cos\theta)R^2 + \frac{m_{Cl}}{m}(m_C + m_H)(1 + 2\cos\theta)R^2$$
$$+ \frac{m_H}{m}\{(3m_{Cl} + m_C)R' + 6m_{Cl}R[\tfrac{1}{3}(1 + 2\cos\theta)]^{1/2}\}R'$$

We substitute the following data into the above formulas and then perform the calculations:

$$m_{\rm H} = 1.0078\, m_{\rm u} = 1.0078 \times 1.66054 \times 10^{-27}\ \text{kg}$$

$$m_{\rm Cl} = 34.9688\, m_{\rm u} = 34.9688 \times 1.66054 \times 10^{-27}\ \text{kg}$$

$$m_{\rm C} = 12.0000 \times m_{\rm u} = 12.0000 \times 1.66054 \times 10^{-27}\ \text{kg}$$

$$m = m_{\rm H} + m_{\rm C} + 3m_{\rm Cl} = 117.9142\, m_{\rm u} = 117.9142 \times 1.66054 \times 10^{-27}\ \text{kg}$$

$$R = 177\ \text{pm} = 1.77 \times 10^{-10}\ \text{m}$$

$$R' = 107\ \text{pm} = 1.07 \times 10^{-10}\ \text{m}$$

$$\theta = 110°$$

Since the factor $m_{\rm u}$ is common to each term in the formulas, multiplication by its value need not be performed until the end of the calculation. The results are:

$$I_{\parallel} = 2 \times 34.9688\, m_{\rm u}(1 - \cos 110°) \times (1.77 \times 10^{-10}\ \text{m})^2$$
$$= \boxed{4.88 \times 10^{-45}\ \text{kg m}^2}$$

Substitution of the data in a similar manner into the above formula for $I_{\perp}$ gives

$$\boxed{I_{\perp} = 2.54 \times 10^{-45}\ \text{kg m}^2}$$

We use eqns 12.13 to calculate the rotational constants in wavenumbers.

$$\tilde{A} = \frac{\hbar}{4\pi c I_{\parallel}} = 5.74\ \text{m}^{-1} = \boxed{0.0574\ \text{cm}^{-1}}$$

$$\tilde{B} = \frac{\hbar}{4\pi c I_{\perp}} = 11.02\ \text{m}^{-1} = \boxed{0.1102\ \text{cm}^{-1}}$$

In frequency units we have

$$A = \frac{\hbar}{4\pi I_{\parallel}} = 1.72 \times 10^{9}\ \text{s}^{-1} = \boxed{1.72 \times 10^{9}\ \text{Hz}}$$

$$B = \frac{\hbar}{4\pi I_{\perp}} = 3.30 \times 10^{9}\ \text{s}^{-1} = \boxed{3.30 \times 10^{9}\ \text{Hz}}$$

E12.5(b) The frequency of the transition is related to the rotational constant by

$$h\nu = \Delta E = hc\Delta\tilde{F} = hc\tilde{B}[J(J+1) - (J-1)J] = 2hc\tilde{B}J$$

where J refers to the upper state ($J = 3$). The rotational constant is related to molecular structure by

$$\tilde{B} = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c m_{\rm eff} R^2}$$

where I is moment of inertia, $m_{\rm eff}$ is effective mass, and R is the bond length. Putting these expressions together yields

$$\nu = 2c\tilde{B}J = \frac{\hbar J}{2\pi m_{\rm eff} R^2}$$

The reciprocal of the effective mass is

$$m_{\text{eff}}^{-1} = m_{\text{C}}^{-1} + m_{\text{O}}^{-1} = \frac{(12m_{\text{u}})^{-1} + (15.9949m_{\text{u}})^{-1}}{1.66054\times10^{-27}\,\text{kg}\,m_{\text{u}}^{-1}} = 8.78348\times10^{25}\,\text{kg}^{-1}$$

So, $$\nu = \frac{(8.78348\times10^{25}\,\text{kg}^{-1})\times(1.0546\times10^{-34}\,\text{J s})\times(3)}{2\pi(112.81\times10^{-12}\,\text{m})^2} = \boxed{3.4754\times10^{11}\,\text{s}^{-1}}$$

E12.6(b) (a) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta\tilde{F} = hc\tilde{B}[J(J+1) - (J-1)J] = 2hc\tilde{B}J$$

where J refers to the upper state ($J = 1$). The rotational constant is related to molecular structure by

$$\tilde{B} = \frac{\hbar}{4\pi cI}$$

where I is moment of inertia. Putting these expressions together yields

$$\tilde{\nu} = 2\tilde{B}J = \frac{\hbar J}{2\pi cI}, \quad \text{so} \quad I = \frac{\hbar J}{2\pi c\tilde{\nu}} = \frac{(1.0546\times10^{-34}\,\text{J s})\times(1)}{2\pi(2.998\times10^{10}\,\text{cm s}^{-1})\times(16.93\,\text{cm}^{-1})}$$

$$I = \boxed{3.307\times10^{-47}\,\text{kg m}^2}$$

(b) The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2, \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{H}}^{-1} + m_{\text{Br}}^{-1} = \frac{(1.0078\,m_{\text{u}})^{-1} + (80.9163\,m_{\text{u}})^{-1}}{1.66054\times10^{-27}\,\text{kg}\,m_{\text{u}}^{-1}} = 6.0500\times10^{26}\,\text{kg}^{-1}$$

and $R = \{(6.0494\times10^{26}\,\text{kg}^{-1})\times(3.307\times10^{-47}\,\text{kg m}^2)\}^{1/2}$

$= 1.414\times10^{-10}\,\text{m} = \boxed{141.4\,\text{pm}}$

E12.7(b) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta\tilde{F} = hc\tilde{B}[J(J+1) - (J-1)J] = 2hc\tilde{B}J$$

where J refers to the upper state. So, wavenumbers of adjacent transitions (transitions whose upper states differ by 1) differ by

$$\Delta\tilde{\nu} = 2\tilde{B} = \frac{\hbar}{2\pi cI}, \quad \text{so} \quad I = \frac{\hbar}{2\pi c\Delta\tilde{\nu}}$$

where I is the moment of inertia, m_{eff} is the effective mass, and R is the bond length.

So, $$I = \frac{(1.0546\times10^{-34}\,\text{J s})}{2\pi(2.9979\times10^{10}\,\text{cm s}^{-1})\times(1.033\,\text{cm}^{-1})} = \boxed{5.420\times10^{-46}\,\text{kg m}^2}$$

The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2, \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{F}}^{-1} + m_{\text{Cl}}^{-1} = \frac{(18.9984\, m_{\text{u}})^{-1} + (34.9688\, m_{\text{u}})^{-1}}{1.66054 \times 10^{-27}\,\text{kg}\; m_{\text{u}}^{-1}} = 4.89196 \times 10^{25}\,\text{kg}^{-1}$$

and $R = \{(4.89196 \times 10^{25}\,\text{kg}^{-1}) \times (5.420 \times 10^{-46}\,\text{kg m}^2)\}^{1/2}$

$$= 1.628 \times 10^{-10}\,\text{m} = \boxed{162.8\,\text{pm}}$$

E12.8(b) The rotational constant is

$$\tilde{B} = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c(2m_{\text{O}}R^2)}, \quad \text{so} \quad R = \left(\frac{\hbar}{8\pi c m_{\text{O}}\tilde{B}}\right)^{1/2}$$

where I is the moment of inertia, m_{eff} is the effective mass, and R is the bond length.

$$R = \left(\frac{(1.0546 \times 10^{-34}\,\text{J s})}{8\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (15.9949\, m_{\text{u}}) \times (1.66054 \times 10^{-27}\,\text{kg}\; m_{\text{u}}^{-1})(0.39021)}\right)^{1/2}$$

$$= 1.1621 \times 10^{-10}\,\text{m} = \boxed{116.21\,\text{pm}}$$

E12.9(b) This exercise is analogous to Exercise 12.9(a), but here our solution will employ a slightly different algebraic technique. Let $R = R_{\text{OC}}$, $R' = R_{\text{CS}}$, $\text{O} = {}^{16}\text{O}$, $\text{C} = {}^{12}\text{C}$.

$$I = \frac{\hbar}{4\pi B} \text{ [see the comment after eqn 12.8]}$$

$$I(\text{OC}^{32}\text{S}) = \frac{1.05457 \times 10^{-34}\,\text{J s}}{(4\pi) \times (6.0815 \times 10^{9}\,\text{s}^{-1})} = 1.3799 \times 10^{-45}\,\text{kg m}^2 = 8.3101 \times 10^{-19}\, m_{\text{u}}\,\text{m}^2$$

$$I(\text{OC}^{34}\text{S}) = \frac{1.05457 \times 10^{-34}\,\text{J s}}{(4\pi) \times (5.9328 \times 10^{9}\,\text{s}^{-1})} = 1.4145 \times 10^{-45}\,\text{kg m}^2 = 8.5184 \times 10^{-19}\, m_{\text{u}}\,\text{m}^2$$

The expression for the moment of inertia given in Table 12.1 may be rearranged as follows.

$$\begin{aligned} Im &= m_{\text{A}}mR^2 + m_{\text{C}}mR'^2 - (m_{\text{A}}R - m_{\text{C}}R')^2 \\ &= m_{\text{A}}mR^2 + m_{\text{C}}mR'^2 - m_{\text{A}}^2R^2 + 2m_{\text{A}}m_{\text{C}}RR' - m_{\text{C}}^2R'^2 \\ &= m_{\text{A}}(m_{\text{B}} + m_{\text{C}})R^2 + m_{\text{C}}(m_{\text{A}} + m_{\text{B}})R'^2 + 2m_{\text{A}}m_{\text{C}}RR' \end{aligned}$$

Let $m_{\text{C}} = m_{32\text{S}}$ and $m'_{\text{C}} = m_{34\text{S}}$

$$\frac{Im}{m_{\text{C}}} = \frac{m_{\text{A}}}{m_{\text{C}}}(m_{\text{B}} + m_{\text{C}})R^2 + (m_{\text{A}} + m_{\text{B}})R'^2 + 2m_{\text{A}}RR' \quad \text{(a)}$$

$$\frac{I'm'}{m'_{\text{C}}} = \frac{m_{\text{A}}}{m'_{\text{C}}}(m_{\text{B}} + m'_{\text{C}})R^2 + (m_{\text{A}} + m_{\text{B}})R'^2 + 2m_{\text{A}}RR' \quad \text{(b)}$$

Subtracting

$$\frac{Im}{m_{\text{C}}} - \frac{I'm'}{m'_{\text{C}}} = \left[\left(\frac{m_{\text{A}}}{m_{\text{C}}}\right)(m_{\text{B}} + m_{\text{C}}) - \left(\frac{m_{\text{A}}}{m'_{\text{C}}}\right)(m_{\text{B}} + m'_{\text{C}})\right]R^2$$

Solving for R^2

$$R^2 = \frac{\left(\frac{Im}{m_{\text{C}}} - \frac{I'm'}{m'_{\text{C}}}\right)}{\left[\left(\frac{m_{\text{A}}}{m_{\text{C}}}\right)(m_{\text{B}} + m_{\text{C}}) - \left(\frac{m_{\text{A}}}{m'_{\text{C}}}\right)(m_{\text{B}} + m'_{\text{C}})\right]} = \frac{m'_{\text{C}}Im - m_{\text{C}}I'm'}{m_{\text{B}}m_{\text{A}}(m'_{\text{C}} - m_{\text{C}})}$$

Substituting the masses, with $m_A = m_O$, $m_B = m_C$, $m_C = m_{32S}$, and $m'_C = m_{34S}$

$$m = (15.9949 + 12.0000 + 31.9721)m_u = 59.9670\ m_u$$

$$m' = (15.9949 + 12.0000 + 33.9679)m_u = 61.9628\ m_u$$

$$\begin{aligned} R^2 &= \frac{(33.9679\ m_u) \times (8.3101 \times 10^{-19}\ m_u\ \mathrm{m}^2) \times (59.9670\ m_u)}{(12.0000\ m_u) \times (15.9949\ m_u) \times (33.9679\ m_u - 31.9721\ m_u)} \\ &\quad - \frac{(31.9721\ m_u) \times (8.5184 \times 10^{-19}\ m_u\ \mathrm{m}^2) \times (61.9628\ m_u)}{(12.0000\ m_u) \times (15.9949\ m_u) \times (33.9679\ m_u - 31.9721\ m_u)} \\ &= \frac{51.6446 \times 10^{-19}\ \mathrm{m}^2}{383.071} = 1.3482 \times 10^{-20}\ \mathrm{m}^2 \end{aligned}$$

$$R = 1.161\bar{1} \times 10^{-10}\ \mathrm{m} = \boxed{116.1\ \mathrm{pm}} = R_{OC}$$

Because the numerator of the expression for R^2 involves the difference between two rather large numbers of nearly the same magnitude, the number of significant figures in the answer for R is certainly no greater than 4. Having solved for R, either equation (a) or (b) above can be solved for R'. The result is

$$R' = 1.559 \times 10^{-10}\ \mathrm{m} = \boxed{155.9\ \mathrm{pm}} = R_{CS}$$

E12.10(b) The wavenumber of a Stokes line in rotational Raman is

$$\tilde{\nu}_{\mathrm{Stokes}} = \tilde{\nu}_i - 2\tilde{B}(2J + 3)\ [12.25a]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_{\mathrm{Stokes}} = 20623\ \mathrm{cm}^{-1} - 2(1.4457\ \mathrm{cm}^{-1}) \times [2(2) + 3] = \boxed{20603\ \mathrm{cm}^{-1}}$$

E12.11(b) The separation of lines is $4\tilde{B}$, so $\tilde{B} = \frac{1}{4} \times (3.5312\ \mathrm{cm}^{-1}) = 0.88280\ \mathrm{cm}^{-1}$

Then, we use $R = \left(\dfrac{\hbar}{4\pi m_{\mathrm{eff}} cB}\right)^{1/2}$ [Exercise 12.8(a)]

with $m_{\mathrm{eff}} = \frac{1}{2}m({}^{19}\mathrm{F}) = \frac{1}{2} \times (18.9984\ m_u) \times (1.6605 \times 10^{-27}\ \mathrm{kg}\ m_u^{-1}) = 1.57734\bar{2} \times 10^{-26}\ \mathrm{kg}$

$$\begin{aligned} R &= \left(\frac{1.0546 \times 10^{-34}\ \mathrm{J\ s}}{4\pi(1.577342 \times 10^{-26}\ \mathrm{kg}) \times (2.998 \times 10^{10}\ \mathrm{cm\ s}^{-1}) \times (0.88280\ \mathrm{cm}^{-1})}\right)^{1/2} \\ &= 1.4178\bar{5} \times 10^{-10}\ \mathrm{m} = \boxed{141.78\ \mathrm{pm}} \end{aligned}$$

E12.12(b) The centrifugal distortion constant is given by

$$\tilde{D}_J = \frac{4\tilde{B}^3}{\tilde{\nu}^2}\ [12.17,\ \text{also see Problem 12.21}]$$

$$\tilde{D}_J = \frac{4 \times (0.0809\ \mathrm{cm}^{-1})^3}{(323.2\ \mathrm{cm}^{-1})^2} = \boxed{2.028 \times 10^{-8}\ \mathrm{cm}^{-1}}$$

$$\tilde{D}_J \propto \tilde{B}^3 \quad \tilde{B} \propto \frac{1}{I} \quad I \propto m_{\mathrm{Br}}\ [\text{Table 12.1}]$$

Therefore, $\tilde{D}_J \propto \dfrac{1}{m_{\mathrm{Br}}^3}$ and $\dfrac{\tilde{D}_J(^{81}\mathrm{Br})}{\tilde{D}_J(^{79}\mathrm{Br})} = \dfrac{m_{^{79}\mathrm{Br}}^3}{m_{^{81}\mathrm{Br}}^3} = \dfrac{(78.9183\,m_\mathrm{u})^3}{(80.9163\,m_\mathrm{u})^3} = \boxed{0.9277}$

We have assumed that the internuclear distance remains constant on substitution.

E12.13(b) See eqn 12.22 and Problem 12.26.The most highly populated rotational level is given by

$$J_{\max} \approx \left(\frac{kT}{2hc\tilde{B}}\right)^{1/2} - \frac{1}{2}\,[12.22]$$

For $\mathrm{Br_2}$ after substituting for the constants this expression becomes

$$J_{\max} \approx \left(\frac{T/\mathrm{K}}{0.2328}\right)^{1/2} - \frac{1}{2}$$

(a) At 25°C = 298.15 K, $J_{\max} \approx \left(\dfrac{298.15/\mathrm{K}}{0.2328}\right)^{1/2} - \dfrac{1}{2} \approx \boxed{36}$

(b) At 100°C = 373.15 K, $J_{\max} \approx \left(\dfrac{373.15/\mathrm{K}}{0.2328}\right)^{1/2} - \dfrac{1}{2} \approx \boxed{40}$

Answers are rounded off to the nearest integer.

E12.14(b) The angular frequency is

$$\omega = \left(\frac{k_\mathrm{f}}{m}\right)^{1/2} = 2\pi\nu \quad \text{so} \quad k_\mathrm{f} = (2\pi\nu)^2 m = (2\pi)^2 \times (3.0\ \mathrm{s^{-1}})^2 \times (2.0 \times 10^{-3}\ \mathrm{kg})$$

$$k_\mathrm{f} = \boxed{0.71\ \mathrm{N\ m^{-1}}}$$

E12.15(b) $\omega = \left(\dfrac{k_\mathrm{f}}{m_\mathrm{eff}}\right)^{1/2} \quad \omega' = \left(\dfrac{k_\mathrm{f}}{m'_\mathrm{eff}}\right)^{1/2}$ [prime = $^2\mathrm{H}^{37}\mathrm{Cl}$]

The force constant, k_f, is assumed to be the same for both molecules. The fractional difference is

$$\frac{\omega' - \omega}{\omega} = \frac{\left(\dfrac{k_\mathrm{f}}{m'_\mathrm{eff}}\right)^{1/2} - \left(\dfrac{k_\mathrm{f}}{m_\mathrm{eff}}\right)^{1/2}}{\left(\dfrac{k_\mathrm{f}}{m_\mathrm{eff}}\right)^{1/2}} = \frac{\left(\dfrac{1}{m'_\mathrm{eff}}\right)^{1/2} - \left(\dfrac{1}{m_\mathrm{eff}}\right)^{1/2}}{\left(\dfrac{1}{m_\mathrm{eff}}\right)^{1/2}} = \left(\frac{m_\mathrm{eff}}{m'_\mathrm{eff}}\right)^{1/2} - 1$$

$$\frac{\omega' - \omega}{\omega} = \left(\frac{m_\mathrm{eff}}{m'_\mathrm{eff}}\right)^{1/2} - 1 = \left\{\frac{m_\mathrm{H} m_\mathrm{Cl}}{m_\mathrm{H} + m_\mathrm{Cl}} \times \frac{(m_{^2\mathrm{H}} + m_{^{37}\mathrm{Cl}})}{(m_{^2\mathrm{H}} \cdot m_{^{37}\mathrm{Cl}})}\right\}^{1/2} - 1$$

$$= \left\{\frac{(1.0078\,m_\mathrm{u}) \times (34.9688\,m_\mathrm{u})}{(1.0078\,m_\mathrm{u}) + (34.9688\,m_\mathrm{u})} \times \frac{(2.0140\,m_\mathrm{u}) + (36.9651\,m_\mathrm{u})}{(2.0140\,m_\mathrm{u}) \times (36.9651\,m_\mathrm{u})}\right\}^{1/2} - 1$$

$$= -0.284$$

Thus, the difference is $\boxed{28.4\%}$.

E12.16(b) The fundamental vibrational frequency is

$$\omega = \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu}, \quad \text{so} \quad k_f = (2\pi c\tilde{\nu})^2 m_{\text{eff}}$$

We need the effective mass

$$m_{\text{eff}}^{-1} = m_1^{-1} + m_2^{-1} = (78.9183\ m_u)^{-1} + (80.9163\ m_u)^{-1} = 0.0250298\ m_u^{-1}$$

$$k_f = \frac{[2\pi(2.998\times10^{10}\ \text{cm s}^{-1})\times(323.2\ \text{cm}^{-1})]^2 \times (1.66054\times10^{-27}\ \text{kg}\ m_u^{-1})}{0.0250298\ m_u^{-1}}$$

$$= \boxed{245.9\ \text{N m}^{-1}}$$

E12.17(b) The ratio of the population of the second excited state (N_2) to the first excited state (N_1) is

$$\frac{N_2}{N_1} = \exp\left(\frac{-h\nu}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right)$$

(a) $$\frac{N_2}{N_1} = \exp\left(\frac{-(6.626\times10^{-34}\ \text{J}\ s)\times(2.998\times10^{10}\ \text{cm s}^{-1})\times(321\text{cm}^{-1})}{(1.381\times10^{-23}\ \text{J K}^{-1})\times(298\text{K})}\right) = \boxed{0.212}$$

(b) $$\frac{N_2}{N_1} = \exp\left(\frac{-(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{10}\ \text{cm s}^{-1})\times(321\ \text{cm}^{-1})}{(1.381\times10^{-23}\ \text{J K}^{-1})\times(800\ \text{K})}\right) = \boxed{0.561}$$

E12.18(b) The relationship between vibrational frequency and wavenumber is

$$\omega = \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu}, \quad \text{so} \quad \tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2} = \frac{(k_f m_{\text{eff}}^{-1})^{1/2}}{2\pi c}$$

The effective masses of the hydrogen halides are very similar, but not identical

$$m_{\text{eff}}^{-1} = m_{\text{D}}^{-1} + m_{\text{X}}^{-1}$$

We assume that the force constants as calculated in Exercise 12.18(a) are identical for the deuterium halide and the hydrogen halide.

For DF

$$m_{\text{eff}}^{-1} = \frac{(2.0140\ m_u)^{-1} + (18.9984\ m_u)^{-1}}{1.66054\times10^{-27}\ \text{kg}\ m_u^{-1}} = 3.3071\times10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.3071\times10^{26}\ \text{kg}^{-1})\times(967.04\ \text{kg s}^{-2})\}^{1/2}}{2\pi(2.9979\times10^{10}\ \text{cm s}^{-1})} = \boxed{3002.3\ \text{cm}^{-1}}$$

For DCl

$$m_{\text{eff}}^{-1} = \frac{(2.0140\ m_u)^{-1} + (34.9688\ m_u)^{-1}}{1.66054\times10^{-27}\ \text{kg}\ m_u^{-1}} = 3.1624\times10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.1624\times10^{26}\ \text{kg}^{-1})\times(515.59\ \text{kg s}^{-2})\}^{1/2}}{2\pi(2.9979\times10^{10}\ \text{cm s}^{-1})} = \boxed{2143.7\ \text{cm}^{-1}}$$

For DBr

$$m_{\text{eff}}^{-1} = \frac{(2.0140\, m_{\text{u}})^{-1} + (80.9163\, m_{\text{u}})^{-1}}{1.66054 \times 10^{-27}\ \text{kg}\ m_{\text{u}}^{-1}} = 3.0646 \times 10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0646 \times 10^{26}\ \text{kg}^{-1}) \times (411.75\ \text{kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10}\ \text{cm s}^{-1})} = \boxed{1885.8\ \text{cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1} = \frac{(2.0140\, m_{\text{u}})^{-1} + (126.9045\, m_{\text{u}})^{-1}}{1.66054 \times 10^{-27}\ \text{kg}\ m_{\text{u}}^{-1}} = 3.0376 \times 10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0376 \times 10^{26}\ \text{kg}^{-1}) \times (314.21\ \text{kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10}\ \text{cm s}^{-1})} = \boxed{1640.1\ \text{cm}^{-1}}$$

E12.19(b) Data on three transitions are provided. Only two are necessary to obtain the value of $\tilde{\nu}$ and x_e. The third datum can then be used to check the accuracy of the calculated values.

$$\Delta\tilde{G}(v = 1 \leftarrow 0) = \tilde{\nu} - 2\tilde{\nu}x_e = 2345.15\ \text{cm}^{-1}\ [12.40]$$

$$\Delta\tilde{G}(v = 2 \leftarrow 0) = 2\tilde{\nu} - 6\tilde{\nu}x_e = 4661.40\ \text{cm}^{-1}\ [12.41]$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu} = (3) \times (2345.15\ \text{cm}^{-1}) - (4661.40\ \text{cm}^{-1}) = \boxed{2374.05\ \text{cm}^{-1}}$$

Then, from the first equation

$$x_e = \frac{\tilde{\nu} - 2345.15\ \text{cm}^{-1}}{2\tilde{\nu}} = \frac{(2374.05 - 2345.15)\ \text{cm}^{-1}}{(2) \times (2374.05\ \text{cm}^{-1})} = \boxed{6.087 \times 10^{-3}}$$

x_e data are usually reported as $x_e\tilde{\nu}$, which is

$$x_e\tilde{\nu} = 14.45\ \text{cm}^{-1}$$

$$\begin{aligned}\Delta\tilde{G}(v = 3 \leftarrow 0) = 3\tilde{\nu} - 12vx_e &= (3) \times (2374.05\ \text{cm}^{-1}) - (12) \times (14.45\ \text{cm}^{-1}) \\ &= 6948.74\ \text{cm}^{-1}\end{aligned}$$

which is close to the experimental value.

E12.20(b) $\Delta\tilde{G}_{v+1/2} = \tilde{\nu} - 2(v + 1)x_e\tilde{\nu}$ [12.40], where $\Delta\tilde{G}_{v+1/2} = \tilde{G}(v + 1) - \tilde{G}(v)$

Therefore, since

$$\Delta\tilde{G}_{v+1/2} = (1 - 2x_e)\tilde{\nu} - 2vx_e\tilde{\nu}$$

a plot of $\Delta G_{v+1/2}$ against v should give a straight line, which gives $(1 - 2x_e)\tilde{\nu}$ from the intercept at $v = 0$ and $-2x_e\tilde{\nu}$ from the slope. We draw up the following table:

v	0	1	2	3	4
$\tilde{G}(v)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\tilde{G}_{v+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	

The points are plotted in Figure 12.1.

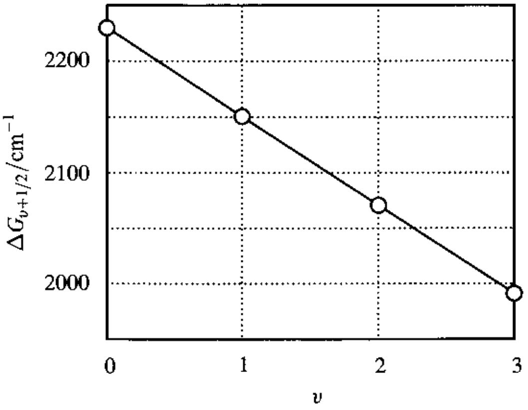


Figure 12.1

The intercept lies at 2230.51 and the slope $= -76.65\ \text{cm}^{-1}$, hence $x_e\tilde{\nu} = 39.83\ \text{cm}^{-1}$.

Since $\tilde{\nu} - 2x_e\tilde{\nu} = 2230.51\ \text{cm}^{-1}$ it follows that $\tilde{\nu} = 2310.16\ \text{cm}^{-1}$.

The dissociation energy may be obtained by assuming that a Morse potential describes the molecule and that the constant $\tilde{D}_e$ in the expression for the potential is an adequate first approximation for it. Then,

$$\tilde{D}_e = \frac{\tilde{\nu}}{4x_e}[12.38] = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} = \frac{(2310.16\ \text{cm}^{-1})^2}{(4)\times(39.83\ \text{cm}^{-1})} = 33.50\times10^3\ \text{cm}^{-1} = 4.15\ \text{eV}$$

However, the depth of the potential well D_e differs from D_0, the dissociation energy of the bond, by the zero-point energy, hence

$$\tilde{D}_0 = \tilde{D}_e - \tfrac{1}{2}\tilde{\nu} = (33.50\times10^3\ \text{cm}^{-1}) - \left(\tfrac{1}{2}\right)\times(2310.16\ \text{cm}^{-1})$$
$$= \boxed{3.235\times10^4\ \text{cm}^{-1}} = \boxed{4.01\ \text{eV}}$$

E12.21(b) The dissociation energy may be obtained by assuming that a Morse potential describes the molecule and that the constant $\tilde{D}_e$ in the expression for the potential is an adequate first approximation for it. Then,

$$\tilde{D}_e = \frac{\tilde{\nu}}{4x_e}[12.38],\ \text{then}\ x_e = \frac{\tilde{\nu}}{4\tilde{D}_e}$$

However, the depth of the potential well $\tilde{D}_e$ differs from $\tilde{D}_0$, the dissociation energy of the bond, by the zero-point energy; hence,

$$\tilde{D}_e = \tilde{D}_0 - \tfrac{1}{2}\tilde{\nu}\ [\text{Figure 12.26}]$$

Data in Table 12.2 for D_0 is given in kJ mol^{-1} and the value for $^1\text{H}^{81}\text{Br}$ is 362.7 kJ mol^{-1}. The conversion factor is 83.593 cm^{-1}/kJ mol^{-1}. Hence,

$$\tilde{D}_e = \tilde{D}_0 + \tfrac{1}{2}\tilde{\nu} = 362.7\ \text{kJ mol}^{-1}\times83.593\ \text{cm}^{-1}/\text{kJ mol}^{-1} + \tfrac{1}{2}\times2648.98\ \text{cm}^{-1} = 31644\ \text{cm}^{-1} = 3.923\ \text{eV}$$

Then, $x_e = \dfrac{\tilde{\nu}}{4\tilde{D}_e} = \dfrac{2648.98\ \text{cm}^{-1}}{4\times31644\ \text{cm}^{-1}} = \boxed{0.02093}$

The anharmonicity constant is inversely proportional to the square root of the effective mass of the molecule since it is proportional to $\tilde{\nu}$ [12.34]

$$x_{\mathrm{e}} \propto \frac{1}{\sqrt{m_{\mathrm{eff}}}}$$

Therefore,

$$\frac{x_{\mathrm{e}}(^{2}\mathrm{H}^{81}\mathrm{Br})}{x_{\mathrm{e}}(^{1}\mathrm{H}^{81}\mathrm{Br})} = \frac{[m_{\mathrm{eff}}(^{1}\mathrm{H}^{81}\mathrm{Br})]^{1/2}}{[m_{\mathrm{eff}}(^{2}\mathrm{H}^{81}\mathrm{Br})]^{1/2}} = \frac{(0.9954\,m_{\mathrm{u}})^{1/2}}{(1.9651\,m_{\mathrm{u}})^{1/2}} = \boxed{0.7117}$$

E12.22(b) The wavenumber of an R-branch infrared transition is

$$\tilde{\nu}_{\mathrm{R}} = \tilde{\nu} + 2\tilde{B}(J+1)\ [12.45c]$$

where J is the initial (lower) rotational state. So,

$$\tilde{\nu}_{\mathrm{R}} = 2308.09\ \mathrm{cm}^{-1} + 2(6.511\ \mathrm{cm}^{-1}) \times (2+1) = \boxed{2347.16\ \mathrm{cm}^{-1}}$$

E12.23(b) See Section 12.9. Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The infrared active compounds are

(a) $CH_3\,CH_3$ (b) CH_4 (c) CH_3Cl

COMMENT. A more powerful method for determining infrared activity based on symmetry considerations is described in Section 12.16.

E12.24(b) A non-linear molecule has $3N-6$ normal modes of vibration, where N is the number of atoms in the molecule; a linear molecule has $3N-5$.

(a) C_6H_6 has $3(12)-6=\boxed{30}$ normal modes.

(b) $C_6H_6CH_3$ has $3(16)-6=\boxed{42}$ normal modes.

(c) $HC\equiv C-C\equiv CH$ is linear; it has $3(6)-5=\boxed{13}$ normal modes.

E12.25(b) (a) A planar AB_3 molecule belongs to the $D_{3\mathrm{h}}$ group. Its four atoms have a total of 12 displacements, of which 6 are vibrations. We determine the symmetry species of the vibrations by first determining the characters of the reducible representation of the molecule formed from all 12 displacements and then subtracting from these characters the characters corresponding to translation and rotation. This latter information is directly available in the character table for the group $D_{3\mathrm{h}}$. The resulting set of characters are the characters of the reducible representation of the vibrations. This representation can be reduced to the symmetry species of the vibrations by inspection or by use of the little orthogonality theorem.

$D_{3\mathrm{h}}$	E	σ_{h}	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_{\mathrm{v}}$
χ (translation)	3	1	0	−2	−1	1
Unmoved atoms	4	4	1	1	2	2
χ (total, product)	12	4	0	−2	−2	2
χ (rotation)	3	−1	0	2	−1	−1
χ (vibration)	6	4	0	−2	0	2

χ (vibration) corresponds to $A_1' + A_2'' + 2E'$.

Again referring to the character table of D_{3h}, we see that E′ corresponds to x and y, A_2'' to z, hence $\boxed{\text{A}_2'' \text{ and E}' \text{ are IR active.}}$ We also see from the character table that E′ and A_1' correspond to the quadratic terms; hence $\boxed{\text{A}_1' \text{ and E}' \text{ are Raman active.}}$

(b) A trigonal pyramidal AB_3 molecule belongs to the group C_{3v}. In a manner similar to the analysis in part (a) we obtain

C_{3V}	E	$2C_3$	$3\sigma_V$
χ (total)	12	0	2
χ (vibration)	6	−2	2

χ (vibration) corresponds to $2A_1 + 2E$. We see from the character table that $\boxed{\text{A}_1 \text{ and E}}$ are infrared active and that $\boxed{\text{A}_1 + \text{E}}$ are also Raman active. Thus, all modes are observable in both the infrared and the Raman spectra.

E12.26(b) (b) The boat-like bending of a benzene ring clearly changes the dipole moment of the ring, for the moving of the C–H bonds out of the plane will give rise to a non-cancelling component of their dipole moments. So, the vibration is $\boxed{\text{infrared active}}$.

(a) Since benzene has a centre of inversion, the exclusion rule applies: a mode that is infrared active (such as this one) must be $\boxed{\text{Raman inactive}}$.

E12.27(b) The displacements span $A_{1g} + 2A_{1u} + 2E_{1u} + E_{1g}$. The rotations R_x and R_y span E_{1g}, and the translations span $E_{1u} + A_{1u}$. So the vibrations span $\boxed{A_{1g} + A_{1u} + E_{1u}}$.

Solutions to problems

Solutions to numerical problems

P12.2

$$\tilde{B} = \frac{\hbar}{4\pi c I}\,[12.7]; \quad I = m_{\text{eff}}R^2; \quad R^2 = \frac{\hbar}{4\pi c m_{\text{eff}}\tilde{B}}$$

$$m_{\text{eff}} = \frac{m_\text{C} m_\text{O}}{m_\text{C} + m_\text{O}} = \left(\frac{(12.0000\,m_\text{u}) \times (15.9949\,m_\text{u})}{(12.0000\,m_\text{u}) + (15.9949\,m_\text{u})}\right) \times (1.66054 \times 10^{-27}\,\text{kg}\,m_\text{u}^{-1})$$

$$= 1.13852 \times 10^{-26}\,\text{kg}$$

$$\frac{\hbar}{4\pi c} = 2.79932 \times 10^{-44}\,\text{kg m}$$

$$R_0^2 = \frac{2.79932 \times 10^{-44}\,\text{kg m}}{(1.13852 \times 10^{-26}\,\text{kg}) \times (1.9314 \times 10^2\,\text{m}^{-1})} = 1.2730\bar{3} \times 10^{-20}\,\text{m}^2$$

$$R_0 = 1.1283 \times 10^{-10}\,\text{m} = \boxed{112.83\,\text{pm}}$$

$$R_1^2 = \frac{2.79932 \times 10^{-44}\,\text{kg m}}{(1.13852 \times 10^{-26}\,\text{kg}) \times (1.6116 \times 10^2\,\text{m}^{-1})} = 1.52565 \times 10^{-20}\,\text{m}^2$$

$$R_1 = 1.2352 \times 10^{-10}\,\text{m} = \boxed{123.52\,\text{pm}}$$

COMMENT. The change in internuclear distance is roughly 10%, indicating that the rotations and vibrations of molecules are strongly coupled and that it is an oversimplification to consider them independently of each other.

P12.4 The separations between neighbouring lines are

20.81, 20.60, 20.64, 20.52, 20.34, 20.37, 20.26 mean: 20.51 cm^{-1}

Hence, $\tilde{B} = (\frac{1}{2}) \times (20.51\,\text{cm}^{-1}) = 10.26\,\text{cm}^{-1}$ and

$$I = \frac{\hbar}{4\pi c\tilde{B}} = \frac{1.05457 \times 10^{-34}\,\text{Js}}{(4\pi) \times (2.99793 \times 10^{10}\,\text{cm s}^{-1}) \times (10.26\,\text{cm}^{-1})} = \boxed{2.728 \times 10^{-47}\,\text{kg m}^2}$$

$$R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2} \text{[Table 12.1]} \quad \text{with } m_{\text{eff}} = 1.6266 \times 10^{-27}\,\text{kg [Exercise 12.6(a)]}$$

$$= \left(\frac{2.728 \times 10^{-47}\,\text{kg m}^2}{1.6266 \times 10^{-27}\,\text{kg}}\right)^{1/2} = \boxed{129.5\,\text{pm}}$$

COMMENT. Ascribing the variation of the separations to centrifugal distortion, and not by just taking a simple average, would result in a more accurate value. Alternatively, the effect of centrifugal distortion could be minimized by plotting the observed separations against J, fitting them to a smooth curve, and extrapolating that curve to $J = 0$. Since $\tilde{B} \propto \frac{1}{I}$ and $I \propto m_{\text{eff}}$, $\tilde{B} \propto \frac{1}{m_{\text{eff}}}$. Hence, the corresponding lines in $^2\text{H}^{35}\text{Cl}$ will lie at a factor

$$\frac{m_{\text{eff}}(^1\text{H}^{35}\text{Cl})}{m_{\text{eff}}(^2\text{H}^{35}\text{Cl})} = \frac{1.6266}{3.1622} = 0.5144$$

to low frequency of $^1\text{H}^{35}\text{Cl}$ lines. Hence, we expect lines at $\boxed{42.9, 53.6, 64.2, \ldots\,\text{cm}^{-1}}$.

P12.6 $$R = \left(\frac{\hbar}{4\pi\mu c\tilde{B}}\right)^{1/2} \text{ and } \nu = 2c\tilde{B}(J+1) \quad [12.21\text{a, with } \nu = c\tilde{\nu}]$$

We use $\mu(\text{CuBr}) \approx \dfrac{(63.55) \times (79.91)}{(63.55) + (79.91)} m_u = 35.40\, m_u$

and draw up the following table:

J	13	14	15
ν/MHz	84421.34	90449.25	96476.72
$\tilde{B}/\text{cm}^{-1}$	0.10057	0.10057	0.10057

$$\text{Hence, } R = \left(\frac{1.05457 \times 10^{-34}\,\text{Js}}{(4\pi) \times (35.40) \times (1.6605 \times 10^{-27}\,\text{kg}) \times (2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (0.10057\,\text{cm}^{-1})}\right)^{1/2}$$

$$= \boxed{218\,\text{pm}}$$

P12.8 Plot frequency against J, as in Figure 12.2.

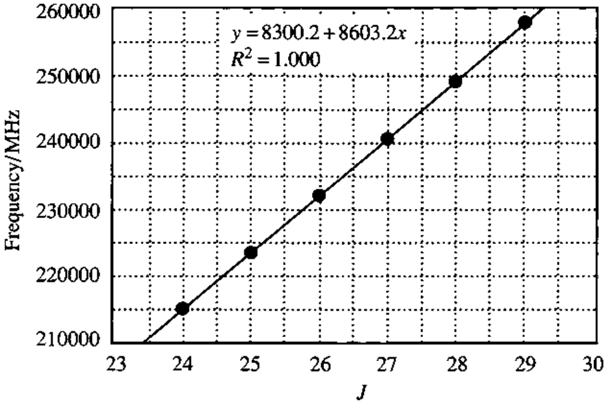


Figure 12.2

The rotational constant is related to the wavenumbers of observed transitions by

$$\tilde{\nu} = 2\tilde{B}(J+1) = \frac{\nu}{c}, \quad \text{so} \quad \nu = 2\tilde{B}c(J+1)$$

A plot of ν versus J, then, has a slope of $2\tilde{B}c$. From Figure 12.2, the slope is 8603 MHz, so

$$\tilde{B} = \frac{8603 \times 10^6\ \text{s}^{-1}}{2(2.988 \times 10^8\ \text{m s}^{-1})} = \boxed{14.35\ \text{m}^{-1}}$$

The most highly populated energy level is roughly

$$J_{\max} = \left(\frac{kT}{2hc\tilde{B}}\right)^{1/2} - \frac{1}{2}$$

$$J_{\max} = \left(\frac{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})}{(6.626 \times 10^{-34}\ \text{J s}) \times (8603 \times 10^6\ \text{s}^{-1})}\right)^{1/2} - \frac{1}{2} = \boxed{26} \text{ at } 298\ \text{K}$$

$$J_{\max} = \left(\frac{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (100\ \text{K})}{(6.626 \times 10^{-34}\ \text{J s}) \times (8603 \times 10^6\ \text{s}^{-1})}\right)^{1/2} - \frac{1}{2} = \boxed{15} \text{ at } 100\ \text{K}$$

P12.10 The Lewis structure is

$$[\ddot{\underset{\cdot\cdot}{O}}{=}N{=}\ddot{\underset{\cdot\cdot}{O}}]^+$$

VSEPR indicates that the ion is $\boxed{\text{linear}}$ and has a centre of symmetry. The activity of the modes is consistent with the rule of mutual exclusion; none is both infrared and Raman active. These transitions may be compared to those for CO_2 (Figure 12.37 of the text) and are consistent with them. The Raman active mode at 1400 cm^{-1} is due to a symmetric stretch ($\tilde{\nu}_1$), that at 2360 cm^{-1} to the antisymmetric stretch ($\tilde{\nu}_3$) and that at 540 cm^{-1} to the two perpendicular bending modes ($\tilde{\nu}_2$). There is a combination band, $\tilde{\nu}_1 + \tilde{\nu}_3 = 3760\ \text{cm}^{-1} \approx 3735\ \text{cm}^{-1}$, which shows a weak intensity in the infrared.

P12.12 $\tilde{D}_0 = \tilde{D}_e - \tilde{\nu}'$ with $\tilde{\nu}' = \frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}$ [Section 12.10]

(a) ^{1}HCl: $\tilde{\nu}' = \{(1494.9) - (\frac{1}{4})\times(52.05)\}$, $\text{cm}^{-1} = 1481.8\ \text{cm}^{-1}$, or 0.184 eV

Hence, $\tilde{D}_0 = 5.33 - 0.18 = \boxed{5.15\ \text{eV}}$

(b) ^{2}HCl: $\dfrac{2m_{\text{eff}}\omega x_e}{\hbar} = a^2$[12.38], so $\tilde{\nu}x_e \propto \dfrac{1}{m_{\text{eff}}}$ as a is a constant. We also have $\tilde{D}_e = \dfrac{\tilde{\nu}^2}{4x_e\tilde{\nu}}$ [Exercise 12.20(a)], so $\tilde{\nu}^2 \propto \dfrac{1}{m_{\text{eff}}}$, implying $\tilde{\nu} \propto \dfrac{1}{m_{\text{eff}}^2}$. Reduced masses were calculated in Exercises 12.18(a) and (b), and we can write

$$\tilde{\nu}(^2\text{HCl}) = \left(\frac{m_{\text{eff}}(^1\text{HCl})}{m_{\text{eff}}(^2\text{HCl})}\right)^{1/2} \times \tilde{\nu}(^1\text{HCl}) = (0.7172)\times(2989.7\ \text{cm}^{-1}) = 2144.2\ \text{cm}^{-1}$$

$$x_e\tilde{\nu}(^2\text{HCl}) = \left(\frac{m_{\text{eff}}(^1\text{HCl})}{m_{\text{eff}}(^2\text{HCl})}\right) \times x_e\tilde{\nu}(^1\text{HCl}) = (0.5144)\times(52.05\ \text{cm}^{-1}) = 26.77\ \text{cm}^{-1}$$

$$\tilde{\nu}'(^2\text{HCl}) = \left(\tfrac{1}{2}\right)\times(2144.2) - \left(\tfrac{1}{4}\right)\times(26.77\ \text{cm}^{-1}) = 1065.4\ \text{cm}^{-1},\quad 0.132\ \text{eV}$$

Hence, $\tilde{D}_0(^2\text{HCl}) = (5.33 - 0.132)\ \text{eV} = \boxed{5.20\ \text{eV}}$

P12.14 (a) In the harmonic approximation

$$\tilde{D}_e = \tilde{D}_0 + \tfrac{1}{2}\tilde{\nu} \quad \text{so} \quad \tilde{\nu} = 2(\tilde{D}_e - \tilde{D}_0)$$

$$\tilde{\nu} = \frac{2(1.51\times10^{-23}\ \text{J} - 2\times10^{-26}\ \text{J})}{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})} = \boxed{152\ \text{m}^{-1}}$$

The force constant is related to the vibrational frequency by

$$\omega = \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2} [12.33] = 2\pi\nu = 2\pi c\tilde{\nu}, \quad \text{so} \quad k_f = (2\pi c\tilde{\nu})^2 m_{\text{eff}}$$

The effective mass is

$$m_{\text{eff}} = \tfrac{1}{2}m = \tfrac{1}{2}(4.003\ m_u)\times(1.66\times10^{-27}\ \text{kg}\ m_u^{-1}) = 3.32\times10^{-27}\ \text{kg}$$

$$k_f = [2\pi(2.998\times10^{8}\ \text{ms}^{-1})\times(152\ \text{m}^{-1})]^2\times(3.32\times10^{-27}\ \text{kg})$$

$$= \boxed{2.72\times10^{-4}\ \text{kg s}^{-2}}$$

The moment of inertia is

$$I = m_{\text{eff}}R_e^2 = (3.32\times10^{-27}\ \text{kg})\times(297\times10^{-12}\ \text{m})^2 = \boxed{2.93\times10^{-46}\ \text{kg m}^2}$$

The rotational constant is

$$\tilde{B} = \frac{\hbar}{4\pi cI} = \frac{1.0546\times10^{-34}\ \text{J s}}{4\pi(2.998\times10^{8}\ \text{ms}^{-1})\times(2.93\times10^{-46}\ \text{kg m}^2)} = \boxed{95.5\ \text{m}^{-1}}$$

(b) In the Morse potential

$$x_e = \frac{\tilde{\nu}}{4\tilde{D}_e} \text{ and } \tilde{D}_e = \tilde{D}_0 + \frac{1}{2}\left(1 - \frac{1}{2}x_e\right)\tilde{\nu} = \tilde{D}_0 + \frac{1}{2}\left(1 - \frac{\tilde{\nu}}{8\tilde{D}_e}\right)\tilde{\nu}$$

This rearranges to a quadratic equation in $\tilde{\nu}$

$$\frac{\tilde{\nu}^2}{16\tilde{D}_e} - \frac{1}{2}\tilde{\nu} + \tilde{D}_e - \tilde{D}_0 = 0, \quad \text{so} \quad \tilde{\nu} = \frac{\frac{1}{2} - \sqrt{(\frac{1}{2})^2 - \frac{4(\tilde{D}_e - \tilde{D}_0)}{16\tilde{D}_e}}}{2(16\tilde{D}_e)^{-1}}$$

$$\tilde{\nu} = 4\tilde{D}_e\left(1 - \sqrt{\frac{\tilde{D}_0}{\tilde{D}_e}}\right)$$

$$= \frac{4(1.51\times10^{-23}\,\mathrm{J})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}\left(1 - \sqrt{\frac{2\times10^{-26}\,\mathrm{J}}{1.51\times10^{-23}\,\mathrm{J}}}\right)$$

$$= \boxed{293\,\mathrm{m^{-1}}}$$

$$\text{and } x_e = \frac{(293\,\mathrm{m^{-1}})\times(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{4(1.51\times10^{-23}\,\mathrm{J})} = \boxed{0.96}$$

P12.16 (a) Follow the flow chart in Figure 11.7 of the text. CH_3Cl is not linear, it has a C_3-axis (only one), it does not have C_2-axes perpendicular to C_3, it has no σ_h, but does have three σ_v planes, so it belongs to $\boxed{C_{3v}}$.

(b) The number of normal modes of a non-linear molecule is $3N - 6$, where N is the number of atoms, so CH_3Cl has $\boxed{\text{nine}}$ normal modes.

(c) To determine the symmetry of the normal modes, consider how the Cartesian axes of each atom are transformed under the symmetry operations of the C_{3v} group; the 15 Cartesian displacements constitute the basis here. All 15 Cartesian axes are left unchanged under the identity, so the character of this operation is 15. Under a C_3 operation, the H atoms are taken into each other, so they do not contribute to the character of C_3. The z-axes of the C and Cl atoms are unchanged, so they contribute 2 to the character of C_3. For these two atoms

$$x \rightarrow -\frac{x}{2} + \frac{3^{1/2}y}{2} \text{ and } y \rightarrow -\frac{y}{2} + \frac{3^{1/2}x}{2},$$

so there is a contribution of $-\frac{1}{2}$ to the character from each of these coordinates in each of these atoms. In total, then $\chi = 0$ for C_3. To find the character of σ_v, call one of the σ_v planes the yz plane; it contains C, Cl, and one H atom. The y and z coordinates of these three atoms are unchanged, but the x coordinates are taken into their negatives, contributing $6 - 3 = 3$ to the character for this operation. The other two atoms are interchanged, so contribute nothing to the character. To find the irreducible representations that this basis spans, we multiply its characters by the characters of the irreducible representations, also multiplying by the number of operations of each kind, sum those products, and divide the sum by the order h of the group (as in Section 11.5(a)). The table below illustrates the procedure.

	E	$2C_3$	$3\sigma_v$		E	$2C_3$	$3\sigma_v$	Sum/h
Basis	15	0	3					
A_1	1	1	1	Basis × A_1	15	0	3	4
A_2	1	1	−1	Basis × A_2	15	0	−3	1
E	2	−1	0	Basis × E	30	0	0	5

Of these 15 modes of motion, three are translations (an A_1 and an E) and three rotations (an A_2 and an E); we subtract these to leave the vibrations, which span

$\boxed{3A_1 + 3E}$ (three A_1 modes, and three doubly degenerate E modes).

(d) Any mode whose symmetry species is the same as that of x, y, or z is infrared active. Thus, $\boxed{\text{all modes are infrared active}}$.

(e) Only modes whose symmetry species is the same as a quadratic form may be Raman active. Thus, $\boxed{\text{all modes are Raman active}}$.

Solutions to theoretical problems

P12.18 The centre of mass of a diatomic molecule lies at a distance x from atom A and is such that the masses on either side of it balance

$$m_A x = m_B(R - x)$$

and hence it is at

$$x = \frac{m_B}{m}R \quad m = m_A + m_B$$

The moment of inertia of the molecule is

$$I = m_A x^2 + m_B(R - x)^2 [12.2] = \frac{m_A m_B^2 R^2}{m^2} + \frac{m_B m_A^2 R^2}{m^2} = \frac{m_A m_B}{m}R^2$$

$$= \boxed{m_{\text{eff}}R^2} \text{ since } m_{\text{eff}} = \frac{m_A m_B}{m_A + m_B}$$

P12.20 The virial theorem states that if the potential energy of a particle has the form $V = ax^b$ then its mean potential and kinetic energies are related by $2\langle E_k\rangle = b\langle V\rangle$ [8.35]. For the harmonic oscillator potential energy $b = 2$ and $\langle E_k\rangle = \frac{1}{2}E_v$ [8.34b] $= \frac{1}{2}(v + \frac{1}{2})\hbar\omega$ [8.24]. Hence, $\langle V\rangle = \langle E_K\rangle = \frac{1}{2}E_v = \frac{1}{2}(v + \frac{1}{2})\hbar\omega$ $= \frac{1}{2}k_f\langle x^2\rangle$ and $\boxed{\langle x^2\rangle = \frac{1}{k_f}(v + \frac{1}{2})\hbar\omega.}$ We see that as v increases, $\langle x^2\rangle$ increases and $\langle R^2\rangle = R_e^2 + \langle x^2\rangle$ [Solution to Problem 12.19] increases. As $\langle R^2\rangle$ increases, the moment of inertia I increases [Table 12.1]. As I increases the $\boxed{\text{rotational constant } B \text{ decreases}}$ [eqn 12.7] as the oscillator is excited to higher quantum states. Anharmonicity results in greater average values of R^2 as v increases [Figure 12.27]; hence, $\boxed{B \text{ decreases with increased anharmonicity}}$.

P12.22 The Morse potential is $V(R) = hc\tilde{D}_e\{1 - e^{-a(R-R_e)}\}^2$ [12.37]. Rewrite this expression as $V(R) = D\{1 - e^{-ax}\}^2$ with $x = R - R_e$ and $D = hc\tilde{D}_e$. The force constant is obtained from

$$k_f = \left(\frac{d^2V}{dx^2}\right)_{x=0} [12.30]$$

$$= \{-2Da(ae^{-ax} - 2ae^{-2ax})\}_{x=0} = \boxed{k_f = 2Da^2.}$$

12.24 The energy levels of a Morse oscillator, expressed as wavenumbers, are given by:

$$\tilde{G}(v) = (v+\tfrac{1}{2})\tilde{\nu} - (v+\tfrac{1}{2})^2 x_e\tilde{\nu} = (v+\tfrac{1}{2})\tilde{\nu} - (v+\tfrac{1}{2})^2\tilde{\nu}^2/4\tilde{D}_e$$

States are bound only if the energy is less than the well depth, $\tilde{D}_e$, also expressed as a wavenumber:

$$\tilde{G}(v) < \tilde{D}_e \quad \text{or} \quad (v+\tfrac{1}{2})\tilde{\nu} - (v+\tfrac{1}{2})^2\tilde{\nu}^2/4\tilde{D}_e < \tilde{D}_e$$

Solve for the maximum value of v by making the inequality into an equality:

$$(v+\tfrac{1}{2})^2\tilde{\nu}^2/4\tilde{D}_e - (v+\tfrac{1}{2})\tilde{\nu} + \tilde{D}_e = 0$$

Multiplying through by $4\tilde{D}_e$ results in an expression that can be factored by inspection into:

$$[(v+\tfrac{1}{2})\tilde{\nu} - 2\tilde{D}_e]^2 = 0 \quad \text{so} \quad v+\tfrac{1}{2} = 2\tilde{D}_e/\tilde{\nu} \quad \text{and} \quad v = \boxed{2\tilde{D}_e/\tilde{\nu} - \tfrac{1}{2}}$$

Of course, v is an integer, so its maximum value is really the greatest integer less than this quantity.

12.26 $N \propto g\mathrm{e}^{-E/kT}$ [Boltzmann distribution, Chapters 2 and 15]

$N_J \propto g_J\mathrm{e}^{-E_J/kT} \propto (2J+1)\mathrm{e}^{-hc\tilde{B}J(J+1)/kT}$ [$g_J = 2J+1$ for a diatomic rotor]

The maximum population occurs when

$$\frac{\mathrm{d}}{\mathrm{d}J}N_J \propto \left\{2 - (2J+1)^2 \times \left(\frac{hc\tilde{B}}{kT}\right)\right\}\mathrm{e}^{-hc\tilde{B}J(J+1)/kT} = 0$$

and, since the exponential can never be zero at a finite temperature, when

$$(2J+1)^2 \times \left(\frac{hc\tilde{B}}{kT}\right) = 2$$

or when $J_{\max} = \boxed{\left(\dfrac{kT}{2hc\tilde{B}}\right)^{1/2} - \dfrac{1}{2}}$

For ICl, with $\dfrac{kT}{hc} = 207.22\ \mathrm{cm^{-1}}$ (inside front cover)

$$J_{\max} = \left(\frac{207.22\ \mathrm{cm^{-1}}}{0.2284\ \mathrm{cm^{-1}}}\right)^{1/2} - \frac{1}{2} = \boxed{30}$$

For a spherical rotor, $N_J \propto (2J+1)^2\mathrm{e}^{-hc\tilde{B}J(J+1)/kT}$ [$g_J = (2J+1)^2$]

and the greatest population occurs when

$$\frac{\mathrm{d}N_J}{\mathrm{d}J} \propto \left(8J + 4 - \frac{hc\tilde{B}(2J+1)^3}{kT}\right)\mathrm{e}^{-hc\tilde{B}J(J+1)/kT} = 0$$

which occurs when

$$4(2J+1) = \frac{hc\tilde{B}(2J+1)^3}{kT}$$

or at $J_{\max} = \boxed{\left(\frac{kT}{hc\tilde{B}}\right)^{1/2} - \frac{1}{2}}$

For CH_4, $J_{\max} = \left(\frac{207.22\ \text{cm}^{-1}}{5.24\ \text{cm}^{-1}}\right)^{1/2} - \frac{1}{2} = \boxed{6}$

Solutions to applications

P12.28 (a) Resonance Raman spectroscopy is preferable to vibrational spectroscopy for studying the O–O stretching mode because such a mode would be $\boxed{\text{infrared inactive}}$, or at best only weakly active. (The mode is sure to be inactive in free O_2 because it would not change the molecule's dipole moment. In a complex in which O_2 is bound, the O–O stretch may change the dipole moment, but it is not certain to do so at all, let alone strongly enough to provide a good signal.)

(b) The vibrational wavenumber is proportional to the frequency, and it depends on the effective mass as follows,

$$\tilde{\nu} \propto \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2}, \quad \text{so} \quad \frac{\tilde{\nu}(^{18}O_2)}{\tilde{\nu}(^{16}O_2)} = \left(\frac{m_{\text{eff}}(^{16}O_2)}{m_{\text{eff}}(^{18}hrmO_2)}\right)^{1/2} = \left(\frac{16.0\ m_u}{18.0\ m_u}\right)^{1/2} = 0.943,$$

and $\tilde{\nu}(^{18}O_2) = (0.943)(844\ \text{cm}^{-1}) = \boxed{796\ \text{cm}^{-1}.}$

Note the assumption that the effective masses are proportional to the isotopic masses. This assumption is valid in the free molecule, where the effective mass of O_2 is equal to half the mass of the O atom; it is also valid if the O_2 is strongly bound at one end, such that one atom is free and the other is essentially fixed to a very massive unit.

(c) The vibrational wavenumber is proportional to the square root of the force constant. The force constant is itself a measure of the strength of the bond (technically of its stiffness, which correlates with strength), which in turn is characterized by bond order. Simple molecular orbital analysis of O_2, O_2^-, and O_2^{2-} results in bond orders of $\boxed{\text{2, 1.5, and 1, respectively}}$. Given decreasing bond order, one would expect decreasing vibrational wavenumbers (and vice versa).

(d) The wavenumber of the O – O stretch is very similar to that of the peroxide anion, suggesting $\boxed{Fe_2^{3+}O_2^{2-}}$.

(e) The detection of two bands due to $^{16}O^{18}O$ implies that the two O atoms occupy non-equivalent positions in the complex. Structures **9** and **10** are consistent with this observation, but structures **7** and **8** are not.

P12.30 The question of whether to use CN or CH within the interstellar cloud of constellation Ophiuchus for the determination of the temperature of the cosmic background radiation depends on which one has a rotational spectrum that best spans black-body radiation of 2.726 K. Given $\tilde{B}_0(CH) = 14.190\ \text{cm}^{-1}$, the rotational constant that is needed for the comparative analysis may be calculated from the 226.9-GHz spectral line of the Orion Nebula. Assuming that the line is for the $^{12}C^{14}N$ isotopic species and $J+1 \leftarrow J = 1$, which gives a reasonable estimate of the CN bond length (117.4 pm), the CN rotational constant is calculated as follows.

$$\tilde{B}_0 = B/c = \frac{\nu}{2c(J+1)} = \frac{\nu}{4c}$$
$$= 1.892\ \text{cm}^{-1}$$

Black-body radiation at 2.726 K may be plotted against radiation wavenumber with suitable transformation of eqn 7.8.

$$\rho(\tilde{\nu}) = \frac{8\pi hc\tilde{\nu}^3}{e^{hc\tilde{\nu}/kT} - 1}$$

Spectral absorption lines of $^{12}C^{14}N$ and $^{12}C^1N$ are calculated with eqn 12.21a.

$$\tilde{\nu}(J+1 \leftarrow J) = 2\tilde{B}(J+1) \quad J = 0, 1, 2, 3 \ldots$$

The cosmic background radiation and molecular absorption lines are shown in Figure 12.3. It is evident that only CN spans the background radiation.

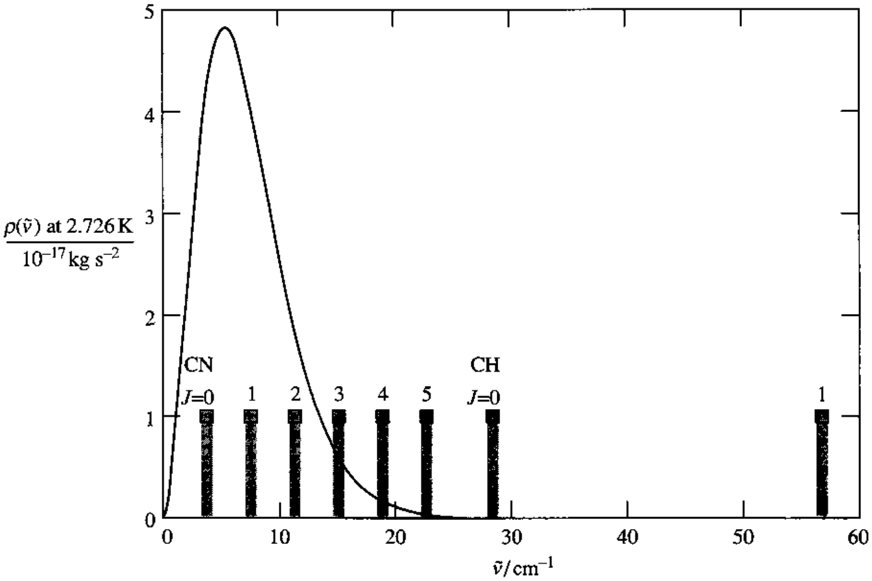


Figure 12.3

P12.32 (a) The H_3^+ molecule is held together by a two-electron, three-centre bond, and hence its structure is expected to be an equilateral triangle. Looking at Figure 12.4 and using the law of cosines

$$R^2 = 2R_C^2 - 2R_C^2\cos(180° - 2\theta)$$
$$= 2R_C^2(1 - \cos(120°)) = 3R_C^2$$

Therefore,

$$R_C = R/\sqrt{3}$$
$$I_C = 3mR_C^2 = 3m(R/\sqrt{3})^2 = mR^2$$
$$I_B = 2mR_B = 2m(R/2)^2 = mR^2/2$$

Therefore,

$$I_C = 2I_B$$

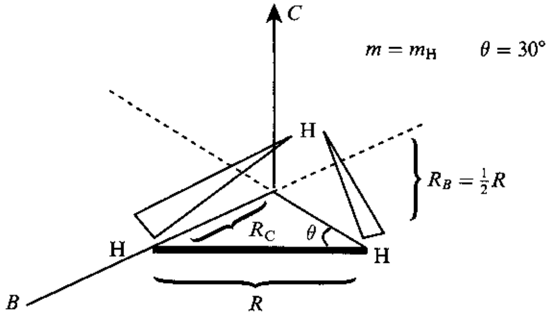


Figure 12.4

(b) $$\tilde{B}=\frac{\hbar}{4\pi c I_B}=\frac{2\hbar}{4\pi c m R^2}=\frac{\hbar}{2\pi c m R^2}\ [12.13]$$

$$R=\left(\frac{\hbar}{2\pi c m \tilde{B}}\right)^{1/2}$$

$$=\left(\frac{\hbar N_A}{2\pi c M_H \tilde{B}}\right)^{1/2}\left(\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times(\frac{10^{-2}\,\mathrm{m}}{\mathrm{cm}})}{2\pi(2.998\times10^{8}\,\mathrm{m\,s^{-1}})\times(0.001008\,\mathrm{kg\,mol^{-1}})\times(43.55\,\mathrm{cm^{-1}})}\right)^{1/2}$$

$$=8.764\times10^{-11}\,\mathrm{m}=\boxed{87.86\ \mathrm{pm}}$$

Alternatively, the rotational constant $\tilde{C}$ can be used to calculate R.

$$\tilde{C}=\frac{\hbar}{4\pi c I_C}=\frac{\hbar}{4\pi c m R^2}\ [12.13]$$

$$R=\left(\frac{\hbar}{4\pi c m \tilde{C}}\right)^{1/2}=\left(\frac{\hbar N_A}{4\pi c M_H \tilde{C}}\right)^{1/2}$$

$$=\left(\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times(\frac{10^{-2}\,\mathrm{m}}{\mathrm{cm}})}{4\pi(2.998\times10^{8}\,\mathrm{m\,s^{-1}})\times(0.001008\,\mathrm{kg\,mol^{-1}})\times(20.71\,\mathrm{cm^{-1}})}\right)$$

$$=8.986\times10^{-11}\,\mathrm{m}=\boxed{89.86\ \mathrm{pm}}$$

The values of R calculated with either the rotational constant $\tilde{C}$ or the rotational constant $\tilde{B}$ differ slightly. We approximate the bond length as the average of these two.

$$(R)\approx\frac{(87.64+89.86)\,\mathrm{pm}}{2}=\boxed{88.7\ \mathrm{pm}}$$

(c) $$\tilde{B}=\frac{\hbar}{2\pi c m R^2}=\frac{(1.0546\times10^{-34}\,\mathrm{J}\,s)\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times(\frac{10^{-2}\,\mathrm{m}}{\mathrm{cm}})}{2\pi(2.998\times10^{8}\,\mathrm{m}\,s^{-1})\times(0.001\,008\,\mathrm{kg\,mol^{-1}})\times(87.32\times10^{-12}\,\mathrm{m})^2}$$

$$=\boxed{43.87\ \mathrm{cm^{-1}}}$$

$$\tilde{C}=\tfrac{1}{2}\tilde{B}=\boxed{21.93\ \mathrm{cm^{-1}}}$$

(d) $\dfrac{1}{m_{\text{eff}}} = \dfrac{3}{m}$ or $m_{\text{eff}} = \frac{1}{3}m$

Since $m_{\text{D}} = 2m_{\text{H}}$, $m_{\text{eff,D}} = 2m_{\text{H}}/3$

$$\tilde{\nu}_2(\text{D}_3^+) = \left(\frac{m_{\text{eff}}(\text{H}_3^+)}{m_{\text{eff}}(\text{D}_3^+)}\right)^{1/2} \tilde{\nu}_2(\text{H}_3^+)\ [12.34]$$

$$= \left(\frac{m_{\text{H}}/3}{2m_{\text{H}}/3}\right)^{1/2} \tilde{\nu}_2(\text{H}_3^+) = \frac{\tilde{\nu}_2(\text{H}_3^+)}{2^{1/2}}$$

$$= \frac{2521.6\ \text{cm}^{-1}}{2^{1/2}} = \boxed{1783.0\ \text{cm}^{-1}}$$

Since $\tilde{B}$ and $\tilde{C} \propto \dfrac{1}{m}$, where m = mass of H or D

$$\tilde{B}(\text{D}_3^+) = \tilde{B}(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 43.55\,\text{cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{21.80\ \text{cm}^{-1}}$$

$$\tilde{C}(\text{D}_3^+) = \tilde{C}(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 20.71\ \text{cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{10.37\ \text{cm}^{-1}}$$

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Molecular spectroscopy 2: electronic transitions

Answers to discussion questions

D13.2 The Franck–Condon principle states that, because electrons are so much lighter than nuclei, an electronic transition occurs so rapidly compared to vibrational motions that the internuclear distance is relatively unchanged as a result of the transition. This implies that the most probable transitions $v_f \leftarrow v_i$ are vertical in the sense that bond lengths do not change during the transition. This vertical line (text, Figure 13.7) will, however, intersect any number of vibrational levels v_f in the upper electronic state. Hence, transitions to many vibrational states of the excited state will occur with transition probabilities proportional to the Frank–Condon factors, which are in turn proportional to the overlap integral of the wavefunctions of the initial and final vibrational states. This creates the band structure, a progression of vibrational transitions, that is observed in electronic spectra. The band shape is determined by the relative horizontal positions (text, Figure 13.8) of the two electronic potential energy curves. The most probable absorption transitions are those to excited vibrational states with wavefunctions having a large amplitude at the internuclear position R_e.

Question. You might check the validity of the assumption that electronic transitions are so much faster than vibrational transitions by calculating the time scale of the two kinds of transitions. How much faster is the electronic transition, and is the assumption behind the Franck–Condon principle justified?

D13.4 Colour can arise by emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the electromagnetic spectrum. When a substance emits radiation the perceived colour of the object will be that of the emitted radiation and it may be an additive colour resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its colour is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Scattering, including the diffraction that occurs when light falls on a material with a grid of variation in texture or refractive index having dimensions comparable to the wavelength of light, for example, a bird's plumage, may also form colour.

D13.6 The overall process associated with fluorescence involves the following steps. The molecule is first promoted from the vibrational ground state of a lower electronic level to a higher vibrational–electronic energy level by absorption of energy from a radiation field. Because of the requirements of the Franck–Condon principle, the transition is to excited vibrational levels of the upper electronic state. See text Figures 13.21 and 13.22. Therefore, the absorption spectrum shows a vibrational structure characteristic of the upper state. The excited-state molecule can now lose energy to the surroundings through radiationless transitions and decay to the lowest vibrational level of the upper state. A spontaneous radiative transition now occurs to the lower electronic level and this fluorescence spectrum has a vibrational structure characteristic of the lower state. The fluorescence spectrum is not the mirror image of the absorption spectrum because the vibrational frequencies of the upper and lower states are different due to the difference in their potential energy curves.

13.8 (a) Continuous-wave (CW) laser emission is possible when heat is easily dissipated and population inversion can be continuously maintained by pumping. The red laser pointer is an example of a CW laser. Typically, the light amplification by stimulated emission of radiation is continuous in the optical cavity and one of the two mirrors, the output coupler, at the ends of the cavity is partially transparent so that only a fraction of the cavity radiation can continuously escape. The gain medium is pumped to the excited state by electricity, a flash lamp, or another laser.

(b) The pulsed laser periodically emits a pulse of high peak power radiation, which is much higher than can be achieved with a CW laser because the average laser power is released in a pulse of short duration. Pulses may be achieved by Q-switching or mode locking. In Q-switching, the laser cavity resonance characteristics are modified to make the cavity conditions unfavourable for lasing, during which time a healthy population inversion is achieved; the cavity is then suddenly brought to resonance, releasing the radiation pulse. The electro-optical Pockels cell or a saturable absorber may be used as Q-switching devices that give pulses of about 5 ns duration. Picosecond pulses can be achieved by the technique of mode locking in which a range of resonant modes of different frequency are phase locked and superimposed. Interference of the modes gives rise to short, regular bursts of radiation. Mode locking is achieved by varying the Q-factor of the laser cavity periodically at the frequency $c/2L$. The modulation can be achieved by linking a prism in the cavity to a transducer driven by a radiofrequency source at a frequency $c/2L$. The transducer sets up standing-wave vibrations in the prism and modulates the loss it introduces into the cavity.

Solutions to exercises

E13.1(b) The reduction in intensity obeys the Beer–Lambert law introduced in Section 13.1.

$$\begin{aligned}\log\frac{I}{I_0} &= -\log\frac{I_0}{I} = -\varepsilon[\mathrm{J}]L \text{ [13.3 and 13.4]}\\ &= (-327\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}) \times (2.22\times10^{-3}\ \mathrm{mol\,dm^{-3}}) \times (0.150\ \mathrm{cm})\\ &= -0.109\end{aligned}$$

Hence, $\dfrac{I}{I_0} = 10^{-0.109} = 0.778$, and the reduction in intensity is $\boxed{22.2\ \%}$.

E13.2(b) $$\log\frac{I}{I_0} = -\log\frac{I_0}{I} = -\varepsilon[\mathrm{J}]L \text{ [13.3, 13.4]}$$

Hence, $\varepsilon = -\dfrac{1}{[\mathrm{J}]L}\log\dfrac{I}{I_0} = -\dfrac{\log(0.655)}{(6.67\times10^{-4}\ \mathrm{mol\,dm^{-3}})\times(0.35\ \mathrm{cm})} = 7.9\times10^{2}\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$

$$(7.9\times10^{2}\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}})\times(10\ \mathrm{cm\,dm^{-1}})^3 = \boxed{7.9\times10^{5}\ \mathrm{cm^2\,mol^{-1}}}$$

E13.3(b) $\log T = -A = -\varepsilon[\mathrm{J}]L$ [13.2, 13.3, 13.4]

$$[\mathrm{J}] = -\frac{1}{\varepsilon L}\log T = \frac{-\log(1-0.523)}{(323\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}})\times(0.750\ \mathrm{cm})}$$

$$= \boxed{1.33\ \mathrm{mmol\ dm^{-3}}}$$

E13.4(b) A parabolic lineshape is symmetrical, extending an equal distance on either side of its peak. It is well known, and proven in the note below, that the area under a parabola equals $\frac{2}{3}$ × base width × height. Let $\tilde{\nu}_i$ and $\tilde{\nu}_f$ be the initial and final wavenumbers of the absorption band. Then, the base of the band has the width $\Delta\tilde{\nu} = \tilde{\nu}_f - \tilde{\nu}_i$ and the integrated absorption coefficient is the area given by

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\ [13.5] = \int_{\tilde{\nu}_i}^{\tilde{\nu}_f} \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu} = \tfrac{2}{3}\times(\tilde{\nu}_f - \tilde{\nu}_i)\times\varepsilon_{\max}$$

Since $\tilde{\nu} = \lambda^{-1}$ and $\tilde{\nu}/\mathrm{cm^{-1}} = 10^7/(\lambda/\mathrm{nm})$,

$$\tilde{\nu}_i/\mathrm{cm^{-1}} = 10^7/(275) = 3.64\times10^4 \quad \text{and} \quad \tilde{\nu}_f/\mathrm{cm^{-1}} = 10^7/(199) = 5.03\times10^4$$

$$\mathcal{A} = \tfrac{2}{3}\times(5.03\times10^4\ \mathrm{cm^{-1}} - 3.64\times10^4\ \mathrm{cm^{-1}})\times(2.25\times10^4\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}})$$

$$= \boxed{2.09\times10^8\ \mathrm{dm^3\,mol^{-1}\,cm^{-2}}}$$

Note: The formula for the area of a parabola can be derived with the equation for a parabola (see Figure 13.40 of the text):

$$\varepsilon(\tilde{\nu}) = \varepsilon_{\max}\{1 - \kappa(\tilde{\nu} - \tilde{\nu}_{\max})^2\}$$

The symmetry of the parabola means that $\tilde{\nu}_{\max} = \tilde{\nu}_i + \frac{1}{2}\Delta\tilde{\nu} = \tilde{\nu}_f - \frac{1}{2}\Delta\tilde{\nu}$. Since $\varepsilon(\tilde{\nu}_i) = \varepsilon(\tilde{\nu}_f) = 0$, the constant κ is easily determined by examination of the parabola equation at either $\varepsilon(\tilde{\nu}_i)$ or $\varepsilon(\tilde{\nu}_f)$:

$$0 = \varepsilon_{\max}\{1 - \kappa(\tilde{\nu}_i - \tilde{\nu}_{\max})^2\} = \varepsilon_{\max}\{1 - \kappa(\tilde{\nu}_i - \tilde{\nu}_i - \tfrac{1}{2}\Delta\tilde{\nu})^2\} = \varepsilon_{\max}\{1 - \tfrac{1}{4}\kappa\Delta\tilde{\nu}^2\} \quad \text{or} \quad \kappa = \frac{4}{\Delta\tilde{\nu}^2}$$

Thus,

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\ [13.5] = \int_{\tilde{\nu}_i}^{\tilde{\nu}_f} \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}$$

$$= \varepsilon_{\max}\int_{\tilde{\nu}_i}^{\tilde{\nu}_f}\left\{1 - \frac{4}{\Delta\tilde{\nu}^2}(\tilde{\nu} - \tilde{\nu}_{\max})^2\right\}\mathrm{d}\tilde{\nu} = \varepsilon_{\max}\left[\tilde{\nu} - \frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu} - \tilde{\nu}_{\max})^3\right]_{\tilde{\nu}=\tilde{\nu}_i}^{\tilde{\nu}=\tilde{\nu}_f}$$

$$= \varepsilon_{\max}\left\{\left[\tilde{\nu}_f - \frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}_f - \tilde{\nu}_{\max})^3\right] - \left[\tilde{\nu}_i - \frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}_i - \tilde{\nu}_{\max})^3\right]\right\}$$

$$= \varepsilon_{\max}\left\{\left[\tilde{\nu}_f - \frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}_f - (\tilde{\nu}_f - \tfrac{1}{2}\Delta\tilde{\nu}))^3\right] - \left[\tilde{\nu}_i - \frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}_i - (\tilde{\nu}_i + \tfrac{1}{2}\Delta\tilde{\nu}))^3\right]\right\}$$

$$= \varepsilon_{\max}\left\{\left[\tilde{\nu}_f - \frac{\Delta\tilde{\nu}}{6}\right] - \left[\tilde{\nu}_i + \frac{\Delta\tilde{\nu}}{6}\right]\right\} = \tfrac{2}{3}\times\Delta\tilde{\nu}\times\varepsilon_{\max}$$

Note: The given data are not consistent with a parabolic lineshape when plotted as a function of either wavelength or wavenumber, for the peak does not fall at the centre of either the wavelength or the wavenumber range. The integrated absorption coefficient can be estimated with the given data assuming a triangular lineshape as a function of wavenumber. If the peak is triangular, the area is

$$\begin{aligned}\mathcal{A} &= \tfrac{1}{2}(\text{base}) \times (\text{height})\\ &= \tfrac{1}{2}[(199 \times 10^{-9}\,\text{m})^{-1} - (275 \times 10^{-9}\,\text{m})^{-1}] \times (2.25 \times 10^{4}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})\\ &= 1.5\overline{6} \times 10^{10}\,\text{dm}^3\,\text{m}^{-1}\,\text{mol}^{-1}\,\text{cm}^{-1} = \frac{(1.5\overline{6} \times 10^{9}\,\text{dm}^3\,\text{m}^{-1}\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (100\,\text{cm m}^{-1})}{10^3\,\text{dm}^3\,\text{m}^{-3}}\\ &= 1.5\overline{6} \times 10^{9}\,\text{m mol}^{-1} = 1.5\overline{6} \times 10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-2}\end{aligned}$$

E13.5(b) $$\varepsilon = -\frac{1}{[\text{J}]L}\log\frac{I}{I_0}\,[13.3, 13.4] \quad \text{with } L = 0.250\,\text{cm}$$

We use this formula to draw up the following table:

$[\text{dye}]/\text{mol dm}^{-3}$	0.0010	0.0050	0.0100	0.0500	
I/I_0	0.73	0.21	0.042	1.33×10^{-7}	
$\varepsilon/(\text{dm}^{-3}\,\text{mol}^{-1}\,\text{cm}^{-1})$	547	542	551	550	mean: $54\overline{8}$

Hence, the molar absorption coefficient is $\varepsilon = \boxed{5.5 \times 10^{2}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-2}}$.

E13.6(b) $$\varepsilon = -\frac{1}{[\text{J}]L}\log\frac{I}{I_0}\,[13.3, 13.4] = \frac{-1}{(0.0155\,\text{mol dm}^{-3}) \times (0.250\,\text{cm})}\log(0.32) = \boxed{12\overline{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}}$$

The transmittance in a 4.50 mm cell is

$$\begin{aligned}T &= \frac{I}{I_0} = 10^{-[\text{J}]\varepsilon L}\,[13.1, 13.2]\\ &= 10^{(-0.0155\,\text{mol dm}^{-3}) \times (12\overline{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (0.450\,\text{cm})} = 0.079, \text{ or } \boxed{7.9\%}.\end{aligned}$$

E13.7(b) The Beer–Lambert law [13.3, 13.4] is

$$\log\frac{I}{I_0} = -\varepsilon[\text{J}]L \quad \text{so} \quad L[\text{J}] = -\frac{1}{\varepsilon}\log\frac{I}{I_0}$$

(a) $$L[\text{J}] = -\frac{1}{30\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}} \times \log\frac{1}{2} = \boxed{0.010\,\text{mol dm}^{-3}\,\text{cm}}$$

(b) $$L[\text{J}] = -\frac{1}{30\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}} \times \log(0.10) = \boxed{0.033\,\text{mol dm}^{-3}\,\text{cm}}$$

E13.8(b) The integrated absorption coefficient is the area under an absorption peak

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\,\text{d}\tilde{\nu}\,[13.5]$$

We are told that ε is a Gaussian function, i.e. a function of the form

$$\varepsilon = \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right)$$

where $x = \tilde{\nu} - \tilde{\nu}_{\max}$ and a is a parameter related to the width of the peak. The integrated absorption coefficient, then, is

$$\mathcal{A} = \int_{-\infty}^{\infty} \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right) \mathrm{d}x = \varepsilon_{\max} a \sqrt{\pi}$$

We must relate a to the half-width at half-height, $x_{1/2}$:

$$\tfrac{1}{2}\varepsilon_{\max} = \varepsilon_{\max} \exp\left(\frac{-x_{1/2}^2}{a^2}\right), \quad \text{so} \quad \ln\tfrac{1}{2} = \frac{-x_{1/2}^2}{a^2} \quad \text{and} \quad a = \frac{x_{1/2}}{\sqrt{\ln 2}}$$

So, $$\mathcal{A} = \varepsilon_{\max} x_{1/2} \left(\frac{\pi}{\ln 2}\right)^{1/2} = (1.54 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}) \times (4233\ \mathrm{cm^{-1}}) \times \left(\frac{\pi}{\ln 2}\right)^{1/2}$$

$$= \boxed{1.39 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}}$$

E13.9(b) The valence ground electronic state of the dinitrogen cation is $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1$ (see Figure 10.34 of the text), which has the term symbol $^2\Sigma_g^+$. We guess that the excited state may be $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 1\pi_g^1$ and check that this state has the term $^2\Pi_g$. First, the only unpaired electron in this excited state is $1\pi_g^1$. This has the desired spin multiplicity of two because $2S + 1 = 2s_1 + 1 = 2(\frac{1}{2}) + 1 = 2$. This excited state also has the desired value of the total orbital angular momentum around the molecular axis ($|\Lambda| = 1$) because the sum of the λ values for the filled $1\sigma_g^2$, $1\sigma_u^2$, and $1\pi_u^4$ levels is zero and, consequently, the angular momentum projection on the molecular axis is that of the $1\pi_g^1$ electron alone. Finally, this excited state has the overall gerade parity because the parity of the filled level is g and the parity of the $1\pi_g^1$ electron is g, from which we find that the overall parity is g × g = g. Since the excited state $\boxed{1\sigma_g^2 1\sigma_u^2 1\pi_u^4 1\pi_g^1}$ has the desired properties, it is a $^2\Pi_g$ term.

E13.10(b) The $1\sigma_g^2 1\sigma_u^2 1\pi_u^2 1\pi_g^2$ valence configuration has four unpaired electrons because both the $1\pi_u$ and $1\pi_g$ levels are doubly degenerate (see text Figure 10.33), each with two electrons in parallel according to Hund's rules. Thus, $S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$ and the spin multiplicity is given by $2S + 1 = 2(2) + 1 = \boxed{5}$. Because u × u = g and g × g = g, the net parity of two electrons paired in an orbital is always gerade. Consequently, the overall parity is found by multiplying the parity of unpaired electrons. For this configuration, u × u × g × g = $\boxed{\mathrm{g}}$.

E13.11(b) The electronic spectrum selection rules concerned with changes in angular momentum are (Section 13.2(b)): $\Delta\Lambda = 0, \pm 1$ $\quad \Delta S = 0 \quad \Delta\Sigma = 0 \quad \Delta\Omega = 0, \pm 1$, where $\Omega = \Lambda + \Sigma$. Λ gives the total orbital angular momentum about the internuclear axis and Σ gives the total spin angular momentum about the internuclear axis. The ± superscript selection rule for reflection in the plane along the internuclear axis is $+\leftrightarrow+$ or $-\leftrightarrow-$ (i.e. $+\leftrightarrow-$ is forbidden). The **Laporte selection rule** states that for a centrosymmetric molecule (those with a centre of inversion) the only allowed transitions are transitions that are accompanied by a change of parity: u↔g.

(a) The changes in the transition ${}^1\Sigma_g^+ \leftrightarrow {}^1\Sigma_u^+$ are $\Delta\Lambda = 0$, $\Delta S = 0$, $\Delta\Sigma = 0$, $\Delta\Omega = 0$, u↔g, and +↔+ so the transition is $\boxed{\text{allowed}}$.

(b) The changes in the transition ${}^3\Sigma_g^+ \leftrightarrow {}^3\Sigma_u^+$ are $\Delta\Lambda = 0$, $\Delta S = 0$, $\Delta\Sigma = 0$, $\Delta\Omega = 0$, u↔g, and +↔+ so the transition is $\boxed{\text{allowed}}$.

(c) Parity does not change in the transition $t_{2g} \leftrightarrow e_g$ so the transition is $\boxed{\text{forbidden}}$. However, this transition is often observed because of either the presence of asymmetric vibrations or the Jahn–Teller effect.

(d) The transition $\pi^* \leftrightarrow n$ is $\boxed{\text{forbidden}}$, for example in a carbonyl group, because the non-bonding orbital of the lone pair on the oxygen does not change sign (+) under reflection in the plane that contains the σ bond, while the π* orbital does change sign (–). The +↔– transition is forbidden.

E13.12(b) We begin by evaluating the normalization constants N_0 and $N_{1'}$.

$$N_0^2 = \frac{1}{\displaystyle\int_{-\infty}^{\infty} e^{-2ax^2}\,dx} = \left(\frac{2a}{\pi}\right)^{1/2} \text{ (standard integral);} \quad N_0 = \left(\frac{2a}{\pi}\right)^{1/4}$$

Likewise, $$N_{1'}^2 = \frac{1}{\displaystyle\int_{-\infty}^{\infty} x^2 e^{-2b(x-x_0)^2}\,dx} = \frac{(2b)^{3/2}}{\Gamma(3/2)} = \frac{(2b)^{3/2}}{\pi^{1/2}/2}; \quad N_{1'} = \left(\frac{2(2b)^{3/2}}{\pi^{1/2}}\right)^{1/2}$$

Furthermore, we can easily check that

$$ax^2 + b(x - x_0)^2 = z^2 + \frac{ab}{a+b}x_0^2, \quad \text{where} \quad z = (a+b)^{1/2}x - \frac{b}{(a+b)^{1/2}}x_0 \quad \text{and} \quad dx = \frac{1}{(a+b)^{1/2}}dz$$

Then, the vibration overlap integral between the vibrational wavefunction in the upper and lower electronic states is:

$$\begin{aligned}
S(1',0) = \langle 1' | 0 \rangle &= N_0 N_{1'} \int_{-\infty}^{\infty} x e^{-ax^2} e^{-b(x-x_0)^2}\,dx \\
&= N_0 N_{1'} \int_{-\infty}^{\infty} x e^{-\{ax^2 + b(x-x_0)^2\}}\,dx \\
&= \frac{N_0 N_{1'}}{a+b} \int_{-\infty}^{\infty} \left\{\frac{bx_0}{(a+b)^{1/2}} + z\right\} e^{-\left\{z^2 + \frac{ab}{a+b}x_0^2\right\}}\,dz \\
&= \frac{N_0 N_{1'} e^{-\frac{ab}{a+b}x_0^2}}{a+b} \left\{\frac{bx_0}{(a+b)^{1/2}} \int_{-\infty}^{\infty} e^{-z^2}\,dz + \int_{-\infty}^{\infty} z e^{-z^2}\,dz\right\} \\
&= \frac{N_0 N_{1'} e^{-\frac{ab}{a+b}x_0^2}}{a+b} \left\{bx_0 \left(\frac{\pi}{a+b}\right)^{1/2} + \int_{-\infty}^{\infty} z e^{-z^2}\,dz\right\}
\end{aligned}$$

The integral of the above expression is necessarily zero because on the z-axis the function z has ungerade symmetry while the function e^{-z^2} has gerade symmetry. Thus, $\mathrm{u} \times \mathrm{g} = \mathrm{u}$ and the integral over the complete z-axis of an ungerade function equals zero.

$$S(1',0) = \frac{N_0 N_{1'} b x_0 e^{-\frac{ab}{a+b}x_0^2}}{a+b}\left(\frac{\pi}{a+b}\right)^{1/2} = \left(\frac{2a}{\pi}\right)^{1/4}\left(\frac{2(2b)^{3/2}}{\pi^{1/2}}\right)^{1/2}\frac{b x_0 e^{-\frac{ab}{a+b}x_0^2}}{a+b}\left(\frac{\pi}{a+b}\right)^{1/2}$$

$$= \left(\frac{2}{a+b}\right)^{3/2} a^{1/4} b^{7/4} x_0 e^{-\frac{ab}{a+b}x_0^2}$$

For the case $b = a/2$, this simplifies to

$$S(1',0) = \left(\frac{4}{3a}\right)^{3/2} a^{1/4}\left(\frac{a}{2}\right)^{7/4} x_0 e^{-ax_0^2/3} = \left(\frac{32}{729}\right)^{1/4} a^{1/2} x_0 e^{-ax_0^2/3}$$

The Franck–Condon factor is

$$|S(1',0)|^2 = \boxed{\left(\frac{32}{729}\right)^{1/2} a x_0^2 e^{-2ax_0^2/3}}$$

E13.13(b) The rotational constant of the excited state is $\tilde{B}' = 10.470\ \mathrm{cm^{-1}}$ while the rotational constant for the ground state is $\tilde{B} = 10.308\ \mathrm{cm^{-1}}$. Since $\tilde{B}' > \tilde{B}$, the bond length of the excited state is shorter than the equilibrium bond length and the $\boxed{\text{P branch has a band head}}$ (text Figure 13.11b).

P branch ($\Delta J = -1$): $\Delta\tilde{\nu}_P(J) = \tilde{\nu}_P(J) - \tilde{\nu} = -(\tilde{B}' + \tilde{B})J + (\tilde{B}' - \tilde{B})J^2$ [13.11a]

To find the J value at which the head occurs, we need only compute a table of $\Delta\tilde{\nu}_P(J)$ values from low to high J. The point at which $\Delta\tilde{\nu}_P(J)$ is smallest is the branch head.

J	60	61	62	63	64	65	66	67
$\Delta\tilde{\nu}_P(J)/\mathrm{cm^{-1}}$	−663.48	−664.66	−665.51	−666.04	−666.24	−666.12	−665.68	−664.91

As indicated by the table, $\Delta\tilde{\nu}_P(J)$ is a minimum (i.e. the P branch head) when $\boxed{J = 64}$.

An alternative method involves deriving an equation that must be satisfied when $J = J_{\text{head}}$. We start by recognizing that eqn 13.11a indicates that $\Delta\tilde{\nu}_P(J)$ is a quadratic function of J and, in fact, the quadratic shape of the $\tilde{\nu}_P$ against J curve is called the Fortrat parabola. This means that we can derive an equation for J_{head} by finding the maximum of the Fortrat parabola: $\mathrm{d}\Delta\tilde{\nu}_P/\mathrm{d}J = 0$, where $J = J_{\text{head}}$.

$$\frac{\mathrm{d}\Delta\tilde{\nu}_P}{\mathrm{d}J} = \frac{\mathrm{d}}{\mathrm{d}J}\{-(\tilde{B}' + \tilde{B})J + (\tilde{B}' - \tilde{B})J^2\}$$

$$= -(\tilde{B} + \tilde{B}) + 2(\tilde{B}' - \tilde{B})J$$

$$-(\tilde{B}' + \tilde{B}) + 2(\tilde{B}' - \tilde{B})J_{\text{head}} = 0$$

$$J_{\text{head}} = \frac{(\tilde{B}' + \tilde{B})}{2(\tilde{B}' - \tilde{B})} = \frac{(10.470 + 10.308)}{2(10.470 - 10.308)} = 64.13 = 64$$

E13.14(b) The P branch has a band head so we immediately conclude both that the rotational constant of the exited state, $\tilde{B}'$, is greater than the rotational constant of the ground state, $\tilde{B}$, and that the bond length of the excited state is shorter than the equilibrium bond length. Exercise E13.13b demonstrates that the J value of the band head, J_{head}, is the closest integer to $\boxed{\frac{1}{2}(\tilde{B}'+\tilde{B})/(\tilde{B}'-\tilde{B})}$. Thus, if we are only given that $J_{\text{head}} = 25$ and $\tilde{B} = 5.437\ \text{cm}^{-1}$, we know only that

$$24.5 < \tfrac{1}{2}(\tilde{B}'+\tilde{B})/(\tilde{B}'-\tilde{B}) < 25.5$$

because the fractional value of a $\frac{1}{2}(\tilde{B}'+\tilde{B})/(\tilde{B}'-\tilde{B})$ calculation must be rounded-off to give the integer value J_{head}. Algebraic manipulation of the inequality yields

$$\frac{\{2(24.5)+1\}\tilde{B}}{\{2(24.5)-1\}} > \tilde{B}' > \frac{\{2(25.5)+1\}\tilde{B}}{\{2(25.5)-1\}}$$

$$1.042\tilde{B} > \tilde{B}' > 1.040\tilde{B}$$

$$\boxed{5.664\ \text{cm}^{-1} > \tilde{B}' > 5.654\ \text{cm}^{-1}}$$

Here is an alternative solution that gives the same answer with insight into the band head concept. At the head of a P band, $\tilde{\nu}_{J_{\text{head}}+1} > \tilde{\nu}_{J_{\text{head}}}$, where $\tilde{\nu}_{J_{\text{head}}+1}$ is the transition $J_{\text{head}} \leftarrow J = J_{\text{head}}+1$. Substitution of eqn 13.11a into this inequality yields the relationship $\tilde{B}' > (J_{\text{head}}+1)\tilde{B}/J_{\text{head}}$. Similarly, $\tilde{\nu}_{J_{\text{head}}} < \tilde{\nu}_{J_{\text{head}}-1}$ where $\tilde{\nu}_{J_{\text{head}}-1}$ is the transition $J_{\text{head}}-2 \leftarrow J = J_{\text{head}}-1$. Substitution of eqn 13.11a into this inequality yields the relationship $\tilde{B}' < J_{\text{head}}\tilde{B}/(J_{\text{head}}-1)$. Consequently, $(J_{\text{head}}+1)\tilde{B}/J_{\text{head}} < \tilde{B}' < J_{\text{head}}\tilde{B}/(J_{\text{head}}-1)$.

E13.15(b) Modelling the π electrons of 1,3,5-hexatriene as free electrons in a linear box yields non-degenerate energy levels of

$$E_n = \frac{n^2h^2}{8m_eL^2}\ [8.4\text{a}]$$

The molecule has six π electrons, so the lowest-energy transition is from $n = 3$ to $n = 4$. Including half a bond length at each end of the molecule, the length of the box is six times the C–C bond distance d, so

$$\Delta E_{\text{linear}} = \frac{(4^2-3^3)h^2}{8m_e(6d)^2} = \frac{7h^2}{288\,m_ed^2}$$

Modelling the π electrons of benzene as free electrons on a ring of circumference equal to six times the C–C bond distance d, and radius R equal to $3d/\pi$, yields energy levels of

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I}\ [8.38\text{a}]$$

where I is the moment of inertia: $I = m_eR^2$. These energy levels are doubly degenerate, except for the non-degenerate $m_l = 0$. The six π electrons fill the $m_l = 0$ and ±1 levels, so the lowest-energy transition is from $m_l = 1$ to $m_l = 2$:

$$\Delta E_{\text{ring}} = \frac{(2^2-1^2)\hbar^2}{2m_eR^2} = \frac{(2^2-1^2)\hbar^2}{2m_e(3d/\pi)^2} = \frac{h^2}{24\,m_ed^2}$$

Comparing the two shows

$$\Delta E_{\text{linear}} = \frac{7h^2}{288\, m_e d^2} < \Delta E_{\text{ring}} = \frac{h^2}{24\, m_e d^2}$$

Therefore, the lowest-energy absorption will $\boxed{\text{rise}}$ in energy on conversion of 1,3,5-hexatriene to benzene.

E13.16(b) The weak absorption at 320 nm is typical of a carbonyl chromophore of an enol. The assignment is $\pi^*\leftarrow$n, where a non-bonding electron comes from one of the two lone pairs of the oxygen valence. The two lone pairs of oxygen are in sp^2 hybrid orbitals, which define the xy plane that contains the σ bond of the carbonyl. The π^* molecular orbital is perpendicular to this plane. There is little overlap between the n and π^* orbitals, producing a low value for the dipole transition integral and a low molar absorption coefficient.

The strong absorption at 213 nm has the $\pi^*\leftarrow\pi$ assignment. The conjugation of the π bonds of the ethenic chromophore and the carbonyl chromophore causes this transition to be shifted to lower energies with respect to both the $\pi^*\leftarrow\pi$ transition of ethene (165 nm) and the $\pi^*\leftarrow\pi$ transition of propanone (190 nm). This shift can be understood in terms of the simple Hückel theory of π molecular orbitals using the butadiene π energy model shown in text Figure 10.43 and Figure 13.1 below. Figure 13.1 demonstrates a broad principle: the difference between neighbouring energy levels becomes smaller as the number of adjacent, overlapping orbitals becomes larger.

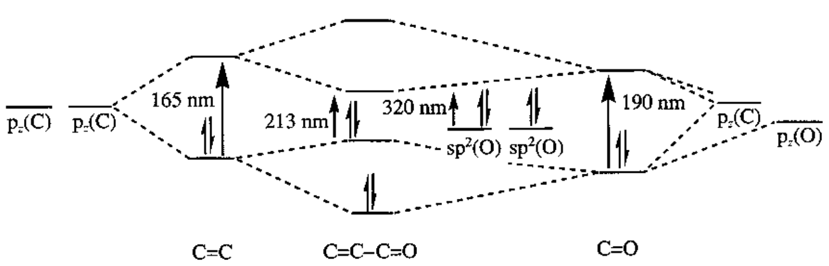


Figure 13.1

E13.17(b) The transition wavenumber is $\tilde{\nu} = \dfrac{1}{\lambda} = \dfrac{1}{305\text{ nm}} = 32.8 \times 10^3\,\text{cm}^{-1}$.

The cyano ligand (CN$^-$) is a strong ligand field splitter, so we expect the d^5 electrons of Fe^{3+} to have the t_{2g}^5 low-spin ground-state configuration in the octahedral $[\text{Fe(CN)}_6]^{3-}$ complex. The d-orbital electron spins are expected to be paired in two of the orbitals of the t_{2g} level with one unpaired electron in the third orbital. This gives $S = 1/2$ and $2S + 1 = 2$ in the ground state. We also expect that $P < \Delta_O$, where P is the energy of repulsion for pairing two electrons in an orbital.

Hypothesis 1. A d–d transition to the $t_{2g}^4 e_g^1$ octahedral excited state with $S = \frac{1}{2}$ and $2S + 1 = 2$ is expected to be parity forbidden and therefore have a small molar absorption coefficient. This transition requires the energy Δ_O and releases the energy P because the excited electron will come from a t_{2g} orbital that has paired electrons in the ground state. Thus, $\tilde{\nu} = \Delta_O - P$ and $\Delta_O = \tilde{\nu} + P$. Using the typical value $P \sim 28 \times 10^3\,\text{cm}^{-1}$ yields the estimate $\Delta_O \sim 61 \times 10^3\,\text{cm}^{-1}$. (See F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn, p. 646, Wiley-Interscience Publishers, New York (1980) for electron-pairing energies.) This Δ_O value is much too large, so we conclude that this transition is unlikely to be a satisfactory description of the observed transition.

Hypothesis 2. Bonding molecular orbitals may form from the LUMOs of the CN^- ligands and the t_{2g} orbitals of Fe^{3+} to produce complex-wide MOs that drastically reduce the electron pairing energy. Using Figure 10.41 (MO diagram of NO) of the text as a model molecular orbital energy diagram for CN^- shows that the cyanide ground electronic configuration is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^0$. It has an antibonding 2π MO LUMO that has the correct symmetry to form a π bond with an Fe^{3+} t_{2g} orbital. This possibility is depicted in Figure 13.2 with the LUMO polarized toward the carbon as expected for an antibonding MO. Overlap of this type will also form complex-wide antibonding π MOs and Figure 13.3 depicts a reasonable energy-level diagram for the complex.

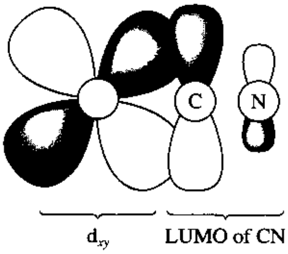


Figure 13.2

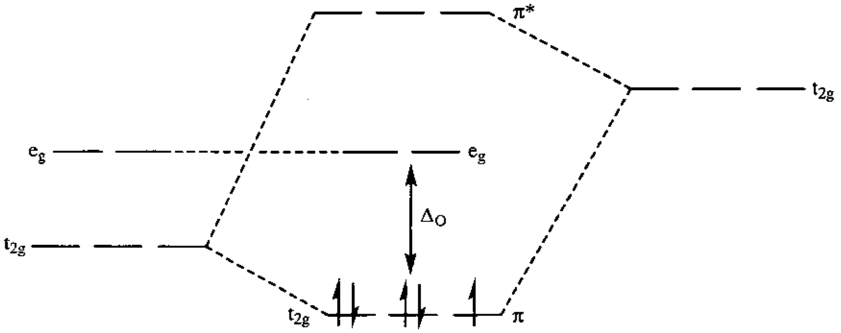


Figure 13.3

As in hypothesis 1, a d–d transition to the $t_{2g}^4 e_g^1$ octahedral excited state with $S = \frac{1}{2}$ and $2S + 1 = 2$ is expected to be parity forbidden and therefore have a small molar absorption coefficient. This transition requires the energy Δ_O and releases the energy P because the excited electron will come from a t_{2g} orbital that has paired electrons in the ground state. Thus, $\tilde{\nu} = \Delta_O - P$ and $\Delta_O = \tilde{\nu} + P$. However, in contrast to hypothesis 1 it now seems reasonable that the complex-wide electron delocalization greatly reduces the electron-pairing energy, making P small enough to ignore. Thus, $\boxed{\Delta_O \sim 33 \times 10^3\,\text{cm}^{-1}}$. This value seems acceptable.

E13.18(b) After some vibrational decay the benzophenone (which does absorb near 360 nm) can transfer its energy to naphthalene. The latter then emits the energy radiatively.

E13.19(b) Only an integral number of half-wavelengths fit into the cavity. These are the **resonant modes.**

$\lambda = 2L/n$ [13.18], where n is an integer and L is the length of the cavity.

The resonant frequencies are given by $\nu = c/\lambda = nc/2L$. The lowest-energy resonant modes ($n = 1$) in a 1.0-m cavity are $\boxed{\lambda = 2.0\text{ m } (\nu = 150\text{ MHz})}$.

E13.20(b) Referring to Example 13.2, we have

$P_{\text{peak}} = E_{\text{pulse}}/t_{\text{pulse}}$ and $P_{\text{average}} = E_{\text{total}}/t = E_{\text{pulse}} \times \nu_{\text{repetition}}$, where $\nu_{\text{repetition}}$ is the pulse repetition rate.

$$t_{\text{pulse}} = E_{\text{pulse}}/P_{\text{peak}} = \frac{20\ \mu\text{J}}{100\ \text{kW}} = \boxed{200\ \text{ps}}$$

$$\nu_{\text{repetition}} = P_{\text{average}}/E_{\text{pulse}} = \frac{0.40\ \text{mW}}{20.0\ \mu\text{J}} = \boxed{20\ \text{Hz}}$$

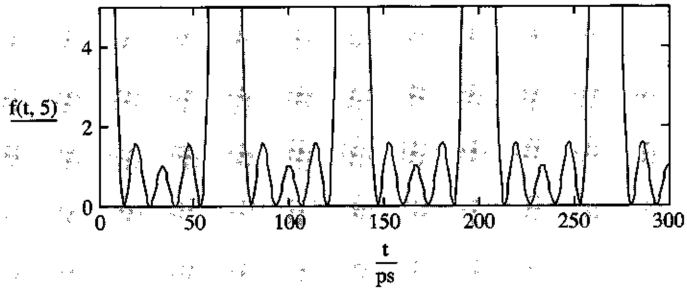
E13.21(b) This Mathcad worksheet simulates the output of a mode-locked laser. The radiation intensity is shown in *Justification* 13.5 to be proportional to the function $f(t,N)$ of the worksheet. The plots demonstrate that the superposition of a great many modes creates very narrow spikes separated by $t = 2L/c$.

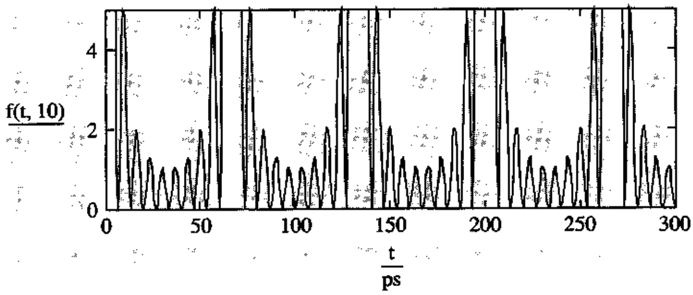
$L := 1.0 \cdot \text{cm}$ $\quad c := 299792458\ \text{m} \cdot \text{s}^{-1}$ $\quad \text{ps} := 10^{-12} \cdot \text{s}$

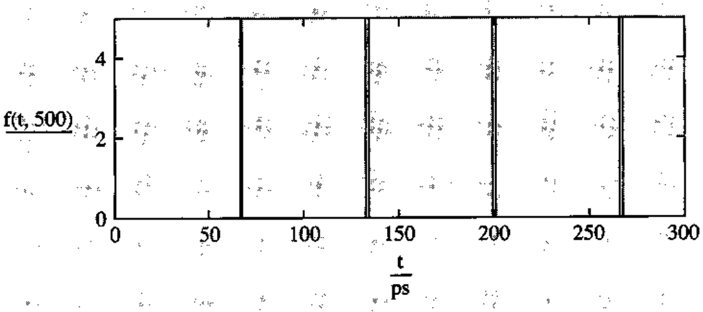
$t_{\text{max}} := 5 \cdot 2 \cdot L \cdot c^{-1}$ $\quad t_{\text{max}} = 333.564\ \text{ps}$

$i_{\text{max}} := 500$ $\quad i := 1 .. i_{\text{max}}$ $\quad t_i := \frac{i \cdot t_{\text{max}}}{i_{\text{max}}}$

$$f(t,N) := \left(\frac{\sin(N \cdot \pi c \cdot t \cdot 2^{-1} \cdot L^{-1})^2}{\sin(\pi c \cdot t \cdot 2^{-1} \cdot L^{-1})}\right)$$







Solutions to problems

Solutions to numerical problems

P13.2 (a) The H_2O^+ vibrational wavenumber (0.41 eV) of the photoelectron spectrum band at 12–13 eV corresponds to about 3300 cm^{-1}, which is close to the 3652 cm^{-1} symmetric stretching mode of the neutral ground state (see text Figure 12.38). This suggests loss of a non-bonding electron. The absence of a long vibrational series in this band is compatible with an ionized equilibrium bond length that approximately equals that of the neutral ground state, thereby producing a large Franck–Condon factor for the adiabatic transition ($v' = 0 \leftarrow v = 0$) and smaller factors for other vibrational transitions ($v' = 1,2, \ldots \leftarrow v = 0$). These observations are compatible with the loss of a non-bonding electron because such a loss does not affect, or has little effect, on the bonding forces constants, vibrational frequencies, or equilibrium bond lengths.

(b) The H_2O^+ vibrational wavenumber (0.125 eV) of the photoelectron spectrum band at 14–16 eV corresponds to about 1000 cm^{-1}, which is very different from the 1595 cm^{-1} bending mode of the neutral ground state (see text Figure 12.38). This suggests loss of a σ bonding electron that severely reduces bond order, a bond force constant, and a vibrational frequency. Consequently, we expect the bond length of the ionized state to be longer than that of the neutral ground state, an observation that is compatible with the long vibrational series of the band because this yields many vertical transitions with significant Franck–Condon factors.

P13.4 The absorption band of text Figure 13.42 appears to be a positively skewed Gaussian with a peak at the point (28 000 cm^{-1}, 9.6 $dm^3\,mol^{-1}\,cm^{-1}$) and half-heights at the points (26 300 cm^{-1}, 4.8 $dm^3\,mol^{-1}\,cm^{-1}$) and (30 200 cm^{-1}, 4.8 $dm^3\,mol^{-1}\,cm^{-1}$). When skew is considered later in this solution, the point (34 000 cm^{-1}, 0.7 $dm^3\,mol^{-1}\,cm^{-1}$) will also be used, but first we note that the low side of the peak appears to have the normal Gaussian shape so we use the half-height on the low side and the peak to estimate the area with a normal Gaussian lineshape having the form

$$\varepsilon = \varepsilon_{\max} e^{-(\tilde{\nu}-\tilde{\nu}_{\text{peak}})^2/a^2}, \quad \text{where } a \text{ is a constant related to the half-width}$$

$$\Delta\tilde{\nu}_{1/2} = 2 \times (28\,000 - 26\,300)\ \text{cm}^{-1} = 3400\ \text{cm}^{-1}$$

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\,d\tilde{\nu}\ [13.5] = \varepsilon_{\max} \int_{-\infty}^{\infty} e^{-(\tilde{\nu}-\tilde{\nu}_{\text{peak}})^2/a^2}\,d\tilde{\nu}$$

$$= \varepsilon_{\max} a\sqrt{\pi} \quad [\text{standard integral}]$$

The relationship between the half-width and a is found by evaluation of the lineshape at $\varepsilon(\tilde{\nu}_{1/2}) = \varepsilon_{\max}/2$:

$$\varepsilon_{\max}/2 = \varepsilon_{\max} e^{-(\tilde{\nu}_{1/2}-\tilde{\nu}_{\text{peak}})^2/a^2}$$

$$\ln(1/2) = -(\tilde{\nu}_{1/2} - \tilde{\nu}_{\text{peak}})^2/a^2$$

$$a^2 = \frac{(\tilde{\nu}_{1/2} - \tilde{\nu}_{\text{peak}})^2}{\ln(2)} = \frac{(\Delta\tilde{\nu}_{1/2}/2)^2}{\ln(2)}$$

$$a = \frac{\Delta\tilde{\nu}_{1/2}}{2\sqrt{\ln 2}}$$

Thus,

$$\mathcal{A} = \boxed{\tfrac{1}{2}\Delta\tilde{\nu}_{1/2}\varepsilon_{\text{max}}\sqrt{\pi/\ln(2)}} = 1.0645\ \Delta\tilde{\nu}_{1/2}\varepsilon_{\text{max}}$$

$$\mathcal{A} = \tfrac{1}{2}(3400\ \text{cm}^{-1}) \times (9.6\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1})\sqrt{\pi/\ln(2)} = \boxed{3.5 \times 10^4\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-2}}$$

The above calculation underestimates the value of $\mathcal{A}$ because the assumption of a normal Gaussian lineshape neglects the fact that text Figure 13.42 shows a band that is obviously skewed toward the higher energies. This increases the area under the curve. In fact, we have calculated the value of $\Delta\tilde{\nu}_{1/2}$ with the value of $\tilde{\nu}_{1/2}$ that comes from the low-energy side of the band because the band appears to be Gaussian when $\tilde{\nu} < \tilde{\nu}_{\text{peak}}$. To account for the tail at higher energy the normal Gaussian lineshape can be multiplied by the function $1 + \text{erf}\left(\dfrac{\tilde{\nu} - c}{b}\right)$, where $\text{erf}(x)$ is the error function (see a mathematics handbook). The parameters $\tilde{\nu}_{\text{peak}}$ and a of the normal Gaussian function are treated as adjustable parameters as are b and c within the error function, that is, the four parameters are adjusted in the sense of a least sum of square errors (SSE) so as to fit the experimental data. The following Mathcad worksheet, which uses the symbol 'v' to represent wavenumber, determines the four parameters.

Estimates of parameters in following equations:

$$\varepsilon_{\text{max}} := 9.6 \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \qquad v_{\text{peak}} := 28000 \cdot \text{cm}^{-1} \qquad a := 2042 \cdot \text{cm}^{-1}$$

$$b := 2000 \cdot \text{cm}^{-1} \qquad c := 28000 \cdot \text{cm}^{-1}$$

Experimental Data:

$$v_{\text{exp}} := \begin{pmatrix} 26300 \\ 28000 \\ 30200 \\ 34000 \end{pmatrix} \cdot \text{cm}^{-1} \qquad \varepsilon_{\text{exp}} := \begin{pmatrix} 4.8 \\ 9.6 \\ 4.8 \\ 0.7 \end{pmatrix} \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$$

Gaussian Distribution of ε:

$$\varepsilon_{\text{Gaussian}}(v, v_{\text{peak}}, a) := \varepsilon_{\text{max}} \cdot e^{\frac{-(v - v_{\text{peak}})^2}{a^2}}$$

Distribution of ε with a akewed Gaussian:

$$\varepsilon(v, v_{\text{peak}}, a, b, c) := \varepsilon_{\text{Gaussian}}(v, v_{\text{peak}}, a) \cdot \left[1 + \text{erf}\left[\frac{(v - c)}{b}\right]\right]$$

Sum of Square Errors function for which constants are adjusted to minimize SSE.

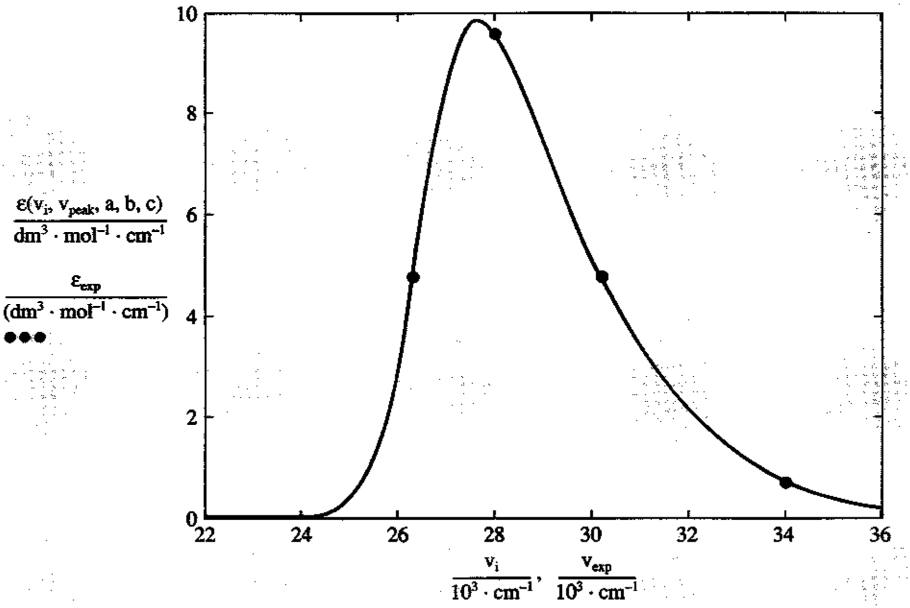
$$\text{SSE}(v_{\text{peak}}, a, b, c) := \sum_{i=0}^{3} \left(\varepsilon_{\text{exp}_i} - \varepsilon(v_{\text{exp}_i}, v_{\text{peak}}, a, b, c)\right)^2$$

Minimization of SSE:

Given $\mathrm{SSE}(v_{peak}, a, b, c) = 0$

$$\begin{pmatrix} v_{peak} \\ a \\ b \\ c \end{pmatrix} := \mathrm{Minerr}(v_{peak}, a, b, c)$$

$v_{peak} = 2.323\times10^4\ \mathrm{cm^{-1}}$ $a = 5.919\times10^3\ \mathrm{cm^{-1}}$ $b = 1.112\times10^3\ \mathrm{cm^{-1}}$ $c = 2.665\times10^4\ \mathrm{cm^{-1}}$



Numerical Integration of Skewed Gaussian Absorption Band:

$$\boxed{\int_{-40000\cdot\mathrm{cm^{-1}}}^{40000\cdot\mathrm{cm^{-1}}} \varepsilon(v, v_{peak}, a, b, c)\,dv = 4.249\times10^4\ \mathrm{dm^3\cdot mol^{-1}\cdot cm^{-2}}}$$

As expected, the integrated absorption coefficient is larger than the value provided by the normal Gaussian estimate. The data fit of the skewed Gaussian, shown in the Mathcad worksheet, is very good.

P13.6 For a photon to induce a spectroscopic transition, the transition moment $\langle\mu\rangle$ must be non-zero, a requirement that leads to electronic spectrum selection rules concerned with changes in angular momentum. The rules for a homonuclear diatomic are (Section 13.2(b)):

$$\Delta\Lambda = 0, \pm1 \quad \Delta S = 0 \quad \Delta\Sigma = 0 \quad \Delta\Omega = 0, \pm1, \quad \text{where } \Omega = \Lambda + \Sigma$$

Λ gives the total orbital angular momentum about the internuclear axis and Σ gives the total spin angular momentum about the internuclear axis. The ± superscript selection rule for reflection in the plane along the internuclear axis is $+\leftrightarrow+$ or $-\leftrightarrow-$ (i.e. $+\leftrightarrow-$ is forbidden). The **Laporte selection rule** states that for a centrosymmetric molecule (those with a centre of inversion) the only allowed transitions are transitions that are accompanied by a change of parity: $u\leftrightarrow g$.

The electric-dipole transition $\boxed{{}^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+ \text{ is allowed}}$ because none of the above rules negate the possibility of this event. You may also wish to reach this conclusion by direct examination of the dipole transition moment integral, $\int \psi_f^* \mu \psi_i \mathrm{d}\tau$, where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation (A_{1g}; see Chapter 11). To find the symmetry species of the integrand, we multiply together the characters of its factors. Homonuclear diatomic molecules and ions belong to the $D_{\infty h}$ point group and the $D_{\infty h}$ character table tells us the symmetry species of each integrand factor.

ψ_f : $A_{1g}(\Sigma_g^+)$
μ_z : $A_{1u}(\Sigma_u^+)$
ψ_i : $A_{1u}(\Sigma_u^+)$

Symmetry product: $A_{1g} \times A_{1u} \times A_{1u} = A_{1g} \times A_{1g} = A_{1g}$

Since the integrand spans A_{1g}, the transition ${}^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$ is allowed.

An electric-dipole transition from a ${}^2\Sigma_u^+$ ground state to a Π_u excited state is forbidden by the Laporte selection rule.

Finally, we check the possibility of a transition from a ${}^2\Sigma_u^+$ ground state to a ${}^2\Pi_g$ excited state by finding whether or not the integrand of the transition integral spans the totally symmetric representation. The symmetry product for the μ_x component is $E_{1g} \times A_{1u} \times A_{1u} = E_{1g} \times A_{1g} = E_{1g}$. Since the integrand does not span A_{1g}, the transition is forbidden for z-polarized light. The symmetry product for both the μ_x and μ_y components is $E_{1g} \times E_{1u} \times A_{1u} = E_{1g} \times E_{1g}$. Since the species product $E_{1g} \times E_{1g}$ has an angular dependence and therefore does not contain the totally symmetric representation, the transition is forbidden for x- and y-polarized light. You may also wish to show this by application of the orthogonality theorem to find the coefficient of A_{1g} in the integrand.

$D_{\infty h}$	E	$\infty C_2'$	$2C_\phi$	i	$\infty\sigma_v$	$2S_\phi$
$\Sigma_u^+(A_{1u})$	1	−1	1	−1	1	−1
μ_x or $\mu_y(E_{1u})$	2	0	$2\cos\phi$	−2	0	$2\cos\phi$
$\Pi_g(E_{1g})$	2	0	$2\cos\phi$	2	0	$-2\cos\phi$
Integrand	4	0	$4\cos^2\phi$	4	0	$4\cos^2\phi$

The orthogonality theorem gives the coefficient of A_{1g} in the integrand as

$$c_{A_{1g}} = (1/h)\Sigma_C g(C)\chi(C) = [4 + 0 + 2(4\cos^2\phi) + 4 + 0 + 2(4\cos^2\phi)]/h$$

Since the group order h, which equals infinity, does not cancel with a numerator factor, $c_{A_{1g}} = 0$.

E13.8 The normalized wavefunctions are:

$$\psi_i = \left(\frac{1}{a}\right)^{1/2} \quad \text{for } 0 \le x \le a \text{ and } 0 \text{ elsewhere}$$

$$\psi_f = \left(\frac{1}{b-\tfrac{1}{2}a}\right)^{1/2} \quad \text{for } \tfrac{1}{2}a \le x \le b \text{ and } 0 \text{ elsewhere}$$

The overlap of these wavefunctions is non-zero in the range $\frac{1}{2}a \le x \le a$ only (assuming that $b \ge a$). Thus, the transition moment is given by

$$\int \psi_f x \psi_i \, dx = \left(\frac{1}{a}\right)^{1/2}\left(\frac{1}{b-\tfrac{1}{2}a}\right)^{1/2}\int_{1/2a}^{a} x\,dx = \left(\frac{1}{a}\right)^{1/2}\left(\frac{1}{b-\tfrac{1}{2}a}\right)^{1/2}\left.\frac{x^2}{2}\right|_{x=1/2a}^{x=a}$$

$$= \left(\frac{1}{a}\right)^{1/2}\left(\frac{1}{b-\tfrac{1}{2}a}\right)^{1/2}\left(\frac{3}{8}a^2\right)$$

$$= \boxed{\frac{3}{8}\left(\frac{a}{b-\tfrac{1}{2}a}\right)^{1/2} a}$$

In the especially symmetric case for which $b = \frac{3}{2}a$: $\int \psi_f x \psi_i \, dx = \frac{3}{8}a$.

P13.10 The ratio of the transition probabilities of spontaneous emission to stimulated emission at a frequency ν is given by

$$A = \left(\frac{8\pi h\nu^3}{c^3}\right)B\,[13.17] = \frac{k}{\lambda^3}B, \text{ where } k \text{ is a constant and we have } \nu = \frac{c}{\lambda}.$$

Thus, at 400 nm $\quad A(400) = \dfrac{k}{(400)^3}B(400),$

and at 500 nm $\quad A(500) = \dfrac{k}{(500)^3}B(500)$

Then, $\dfrac{A(500)}{A(400)} = \left(\dfrac{(400)^3}{(500)^3}\right) \times \left(\dfrac{B(500)}{B(400)}\right) = \left(\dfrac{64}{125}\right) \times 10^{-5} = 5 \times 10^{-6}$

Lifetimes and half-lives are inversely proportional to transition probabilities (rate constants) and hence

$$t_{1/2}(\mathrm{T} \to \mathrm{S}) = \frac{1}{5 \times 10^{-6}} t_{1/2}(\mathrm{S}^* \to \mathrm{S}) = (2 \times 10^5) \times (1.0 \times 10^{-9}\,\mathrm{s}) = \boxed{2 \times 10^{-4}\,\mathrm{s}}$$

P13.12 (a) The molar concentration corresponding to 1 molecule per cubic μm is:

$$\frac{n}{V} = \frac{1}{6.022 \times 10^{23}\,\mathrm{mol^{-1}}} \times \frac{(10^6\,\mu\mathrm{m\,m^{-1}})^3}{(1.0\,\mu\mathrm{m}^3)(10\,\mathrm{dm\,m^{-1}})^3}$$

$$= \boxed{1.7 \times 10^{-9}\,\mathrm{mol\,dm^{-3}} \text{ or } 1.7\,\mathrm{nmol\,dm^{-3}}}$$

(b) An impurity of a compound of molar mass 100 g mol^{-1} present at a concentration of 1.0×10^{-7} kg per 1.00 kg water (i.e. 0.10 μmol kg^{-1}) can be expected to be present at a level of N molecules per cubic μm, where N is:

$$N = \frac{1.0\times10^{-7}\text{ kg impurity}}{1.00\text{ kg water}} \times \frac{6.022\times10^{23}\text{ mol}^{-1}}{100\times10^{-3}\text{ kg impurity mol}^{-1}} \times (1.0\times10^{3}\text{ kg water m}^{-3}) \times (10^{-6}\text{ m})^{3},$$

$$N = \boxed{6.0\times10^{2}}.$$

Pure as it seems, the solvent is much too contaminated for single-molecule spectroscopy.

Solutions to theoretical problems

P13.14 The absorbances A_1 and A_2 at wavelengths λ_1 and λ_2 are the sum of the individual absorbances in the mixture of A and B.

$$A_1 = \varepsilon_{A1}L[\mathrm{A}] + \varepsilon_{B1}L[\mathrm{B}] \quad \text{(i)}$$

$$A_2 = \varepsilon_{A2}L[\mathrm{A}] + \varepsilon_{B2}L[\mathrm{B}] \quad \text{(ii)}$$

Solving (i) for [A] gives

$$[\mathrm{A}] = \frac{A_1 - \varepsilon_{B1}L[\mathrm{B}]}{\varepsilon_{A1}L} \quad \text{(iii)}$$

Substitution of (iii) into (ii) and solving for [B] gives

$$A_2 = \varepsilon_{A2}L\left(\frac{A_1 - \varepsilon_{B1}L[\mathrm{B}]}{\varepsilon_{A1}L}\right) + \varepsilon_{B2}L[\mathrm{B}]$$

$$\varepsilon_{A1}A_2 = \varepsilon_{A2}A_1 - \varepsilon_{A2}\varepsilon_{B1}L[\mathrm{B}] + \varepsilon_{A1}\varepsilon_{B2}L[\mathrm{B}]$$

$$\boxed{[\mathrm{B}] = \frac{\varepsilon_{A1}A_2 - \varepsilon_{A2}A_1}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})L}} \quad \text{(iv)}$$

Substitution of (iv) into (iii) and simplifying gives

$$\varepsilon_{A1}L[\mathrm{A}] = A_1 - \varepsilon_{B1}lL\left\{\frac{\varepsilon_{A1}A_2 - \varepsilon_{A2}A_1}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})L}\right\}$$

$$= \frac{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})A_1 - \varepsilon_{B1}(\varepsilon_{A1}A_2 - \varepsilon_{A2}A_1)}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})}$$

$$= \frac{\varepsilon_{A1}\varepsilon_{B2}A_1 - \varepsilon_{A1}\varepsilon_{B1}A_2}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})}$$

$$\boxed{[\mathrm{A}] = \frac{\varepsilon_{B2}A_1 - \varepsilon_{B1}A_2}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})L}} \quad \text{(v)}$$

Equations (iv) and (v) are the desired results.

P13.16 Use the Clebsch–Gordan series [9.43 and 9.44] to assess both the total orbital and total spin angular momentum quantum numbers. L represents the total orbital angular momentum of an atom; Λ represents the total orbital angular momentum along the internuclear axis of a diatomic molecule.

$$L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \ldots, |l_1 - l_2| \quad [9.43]$$

$$S = s_1 + s_2, s_1 + s_2 - 1, s_1 + s_2 - 2, \ldots, |s_1 - s_2| \quad [9.44]$$

The term symbols for orbital angular momentum are

L or Λ =	0	1	2	3	4	5	6	
	S	P	D	F	G	H	I	for atoms
	Σ	Π	Δ	Φ	Γ	H	I	for diatomic molecules

(a) The ground electronic configuration of dioxygen, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$, is discussed in Section 10.4(d) and the determination of the term symbol, ${}^3\Sigma_g^-$, is described in Section 13.2(a). The triplet spin multiplicity, $2S + 1 = 3$, indicates that $S = 1$. Thus, the sum $S_1 + S_2$ of the dissociated O atom spin quantum numbers must also equal 1. The ground configuration of each O atom, [He]$2s^2 2p^4$ with two unpaired electrons and both S_1 and S_2 equal to 1 by Hund's maximum multiplicity rule for the ground state, satisfies the total spin requirement because the atomic spin alignments are $S_1 + S_2$, $S_1 + S_2 - 1, \ldots |S_1 - S_2|$, which corresponds to 2 or 1(the required value) or 0. With both S_1 and S_2 equal to 1 the spin multiplicity of each atom equals 3 in the ground state. We conclude that the ${}^3\Sigma_g^-$ ground state of O_2 dissociates into O(^{3}P) + O(^{3}P).

The excited $B^3\Sigma_u^-$ state of O_2 dissociates into O(^{3}P) + O(^{1}D), a triplet and a singlet. $S = 1$ for the molecule and the atoms have $S_1 = 1$ and $S_2 = 0$ with the permitted spin alignment of 1. In this case the dissociated atoms have spin multiplicities of 3 and 1.

In summary, we have found the dissociated atomic oxygen spin multiplicity may be either $\boxed{\text{3 and 3}}$ or $\boxed{\text{3 and 1}}$.

(b) The ground electronic configuration of dinitrogen is $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$ and the term symbol is ${}^1\Sigma_g^+$. The singlet spin multiplicity, $2S + 1 = 1$, indicates that $S = 0$. Thus, the sum $S_1 + S_2$ of the dissociated N atom spin quantum numbers must also equal 0. The ground configuration of each N atom, [He]$2s^2 2p^3$ with three unpaired electrons and both S_1 and S_2 equal to $\frac{3}{2}$ by Hund's maximum multiplicity rule for the ground state, satisfies the total spin requirement because the atomic spin alignments are $S_1 + S_2, S_1 + S_2 - 1, \ldots |S_1 - S_2|$, which corresponds to 3 or 2 or 1 or 0(the required value). With both S_1 and S_2 equal to $\frac{3}{2}$ the spin multiplicity of each atom equals 4 in the ground state. We conclude that the ${}^1\Sigma_g^+$ ground state of N_2 dissociates into N(^{4}S) + N(^{4}S).

There are a great many important excited states of dinitrogen. For a summary see Figure 1 in L. Lofthus and P.H. Krupenie, *J. Phy. and Chem. Reference Data*, V. 6 (1), 113–307 (1977), The spectrum of molecular nitrogen (http://www.nist.gov/srd/PDFfiles/jpcrd93.pdf).

The excited $B^3\Sigma_g^-$ state of N_2 dissociates into N(^{4}S) + N(^{2}D), two doublets. $S = 1$ for the molecule and the atoms have $S_1 = \frac{3}{2}$ and $S_2 = \frac{1}{2}$ with alignments of 2 or 1 (the required value). In this case the dissociated atoms have spin multiplicities of 4 and 2.

The excited ${}^3\Pi_g$ state of N_2 dissociates into N(^{2}D) + N(^{2}D), two doublets. $S = 1$ for the molecule and the atoms have $S_1 = \frac{1}{2}$ and $S_2 = \frac{1}{2}$ with the permitted spin alignment of 1. In this case the dissociated atoms have spin multiplicities of 2 and 2.

In summary, we have found the dissociated atomic nitrogen spin multiplicity may be either $\boxed{\text{4 and 4}}$ or $\boxed{\text{4 and 2}}$ or $\boxed{\text{2 and 2}}$.

P13.18 (a) Ethene (ethylene) belongs to D_{2h}. In this group the x, y, and z components of the dipole moment transform as B_{3u}, B_{2u}, and B_{1u}, respectively. The π orbital is B_{1u} (like z, the axis perpendicular to the plane) and π^* is B_{3g}. Since $B_{3g} \times B_{1u} = B_{2u}$ and $B_{2u} \times B_{2u} = A_{1g}$, the transition is $\boxed{\text{allowed}}$ (and is y-polarized).

(b) Regard the CO group with its attached groups as locally C_{2v}. The dipole moment has components that transform as $A_1(z)$, $B_1(x)$, and $B_2(y)$, with the z-axis along the C=O direction and x perpendicular to the R_2CO plane. The n orbital is p_y (in the R_2CO plane), and hence transforms as B_2. The π^* orbital is p_x (perpendicular to the R_2CO plane), and hence transforms as B_1. Since $\Gamma_f \times \Gamma_i = B_1 \times B_2 = A_2$, but no component of the dipole moment transforms as A_2, the transition is $\boxed{\text{forbidden}}$.

P13.20 (a) The Beer–Lambert law is:

$$A = \log\frac{I_0}{I} = \varepsilon[\mathrm{J}]L$$

The absorbed intensity is:

$$I_{\text{abs}} = I_0 - I \quad \text{so} \quad I = I_0 - I_{\text{abs}}$$

Substitute this expression into the Beer–Lambert law and solve for I_{abs}:

$$\log\frac{I_0}{I_0 - I_{\text{abs}}} = \varepsilon[\mathrm{J}]L, \quad \text{so} \quad I_0 - I_{\text{abs}} = I_0 \times 10^{-\varepsilon[\mathrm{J}]L},$$

and $I_{\text{abs}} = \boxed{I_0 \times (1 - 10^{-\varepsilon[\mathrm{J}]L})}$

(b) The problem states that $I_f(\tilde{\nu}_f)$ is proportional to ϕ_f and to $I_{\text{abs}}(\tilde{\nu})$, so:

$$I_f(\tilde{\nu}_f) \propto \phi_f I_0(\tilde{\nu}) \times (1 - 10^{-\varepsilon[\mathrm{J}]L})$$

If the exponent is small, we can expand $1 - 10^{-\varepsilon[\mathrm{J}]L}$ in a power series:

$$10^{-\varepsilon[\mathrm{J}]L} = (e^{\ln 10})^{-\varepsilon[\mathrm{J}]L} \approx 1 - \varepsilon[\mathrm{J}]L \ln 10 + \ldots,$$

and $I_f(\tilde{\nu}_f) \propto \boxed{\phi_f I_0(\tilde{\nu})\varepsilon[\mathrm{J}]L}$

Solutions to applications: biochemistry, environmental science, and astrophysics

P13.22 The fraction of the North Star radiation transmitted to the retina is

$$(1 - 0.30) \times (1 - 0.25) \times (1 - 0.09) \times (1 - 0.43) = 0.27\overline{2}$$

The number of photons focused on the retina in 0.1 s is

$$(0.27\overline{2}) \times (40\ \text{mm}^2) \times (0.1\ \text{s}) \times (4 \times 10^3\ \text{mm}^{-2}\ \text{s}^{-1}) = \boxed{4 \times 10^3}$$

P13.24 The integrated absorption coefficient is

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}\ [13.5]$$

If we can express ε as an analytical function of $\tilde{\nu}$, we can carry out the integration analytically. Following the hint in the problem, we seek to fit ε to an exponential function, which means that a plot of $\ln \varepsilon$ versus $\tilde{\nu}$ ought to be a straight line (Figure 13.4). So, if

$$\ln \varepsilon = m\tilde{\nu} + b, \quad \text{then} \quad \varepsilon = \exp(m\tilde{\nu})\exp(b)$$

and $\mathcal{A} = (\mathrm{e}^{b}/m)\exp(m\tilde{\nu})$ (evaluated at the limits integration). We draw up the following table and find the best-fit line:

λ/nm	ε/(dm^3 mol^{-1} cm^{-1})	$\tilde{\nu}$/cm^{-1}	$\ln \varepsilon$/(dm^3 mol^{-1} cm^{-1})
292.0	1512	34 248	4.69
296.3	865	33 748	4.13
300.8	477	33 248	3.54
305.4	257	32 748	2.92
310.1	135.9	32 248	2.28
315.0	69.5	31 746	1.61
320.0	34.5	31 250	0.912

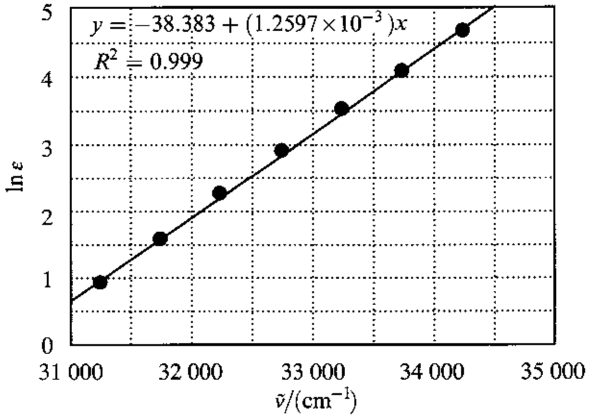


Figure 13.4

$$\text{So,}\quad \mathcal{A} = \frac{\mathrm{e}^{-38.383}}{1.26\times10^{-3}\,\mathrm{cm}}\left[\exp\left(\frac{1.26\times10^{-3}\,\mathrm{cm}}{290\times10^{-7}\,\mathrm{cm}}\right) - \exp\left(\frac{1.26\times10^{-3}\,\mathrm{cm}}{320\times10^{-7}\,\mathrm{cm}}\right)\right]\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$$

$$= \boxed{1.24\times10^{5}\,\mathrm{dm^3\,mol^{-1}\,cm^{-2}}}$$

P13.26 (a) The integrated absorption coefficient is

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}\ [13.5] = \tfrac{1}{2}\varepsilon_{\max}\Delta\tilde{\nu}\ \text{[triangle approx. for area of band]}$$

$$= \tfrac{1}{2}\times(150\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}})\times(34483-31250)\,\mathrm{cm^{-1}} = \boxed{2.42\times10^{5}\,\mathrm{dm^3\,mol^{-1}\,cm^{-2}}}$$

(b) The concentration of gas under these conditions is

$$c = \frac{n}{V} = \frac{p}{RT} = \frac{2.4\ \text{Torr}}{(62.364\ \text{Torr dm}^3\ \text{mol}^{-1}\ \text{K}^{-1}) \times (373\ \text{K})} = 1.03 \times 10^{-4}\ \text{mol dm}^{-3}$$

Over 99% of these gas molecules are monomers, so we take this concentration to be that of CH_3I (If 1 of every 100 of the original monomers turned to dimers, each produces 0.5 dimers; remaining monomers represent 99 of 99.5 molecules.) Beer's law states

$$A = \varepsilon cL = (150\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}) \times (1.03 \times 10^{-4}\ \text{mol dm}^{-3}) \times (12.0\ \text{cm}) = \boxed{0.185}$$

(c) The concentration of gas under these conditions is

$$c = \frac{n}{V} = \frac{p}{RT} = \frac{100\ \text{Torr}}{(62.364\ \text{Torr dm}^3\ \text{mol}^{-1}\ \text{K}^{-1}) \times (373\ \text{K})} = 4.30 \times 10^{-3}\ \text{mol dm}^{-3}$$

Since 18% of these CH_3I units are in dimers (forming 9% as many molecules as were originally present as monomers), the monomer concentration is only 82/91 of this value or 3.87×10^{-3} mol L^{-1}. Beer's law is

$$A = \varepsilon cL = (150\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}) \times (3.87 \times 10^{-3}\ \text{mol dm}^{-3}) \times (12.0\ \text{cm}) = \boxed{6.97}$$

If this absorbance were measured, the molar absorption coefficient inferred from it without consideration of the dimerization would be

$$\varepsilon = A/cL = 6.97/\{(4.30 \times 10^{-3}\ \text{mol dm}^{-3}) \times (12.0\ \text{cm})\} = \boxed{135\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}}$$

an apparent drop of 10% compared to the low-pressure value.

P13.28 The fluorescence spectrum of CN is sketched in Figure 13.5.

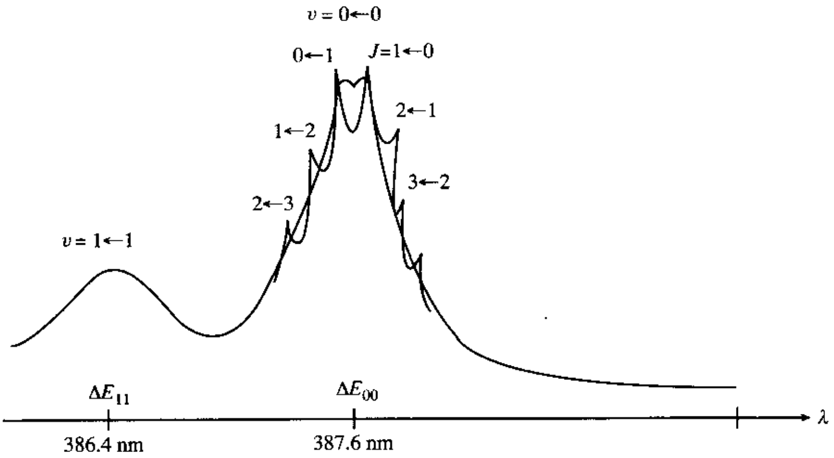


Figure 13.5

$$\Delta E_{11} = \frac{hc}{\lambda_{11}} = \frac{hc}{386.4\ \text{nm}} = 5.1409 \times 10^{-19}\ \text{J} = 3.2087\ \text{eV}$$

and

$$\Delta E_{00} = \frac{hc}{\lambda_{00}} = \frac{hc}{387.6\ \text{nm}} = 5.1250 \times 10^{-19}\ \text{J} = 3.1987\ \text{eV}$$

Energy of excited singlet, $S_1 : E_1(\upsilon, J) = V_1 + (\upsilon + \tfrac{1}{2})\tilde{\nu}_1 hc + J(J+1)\tilde{B}_1 hc$

Energy of ground singlet, $S_0 : E_0(\upsilon, J) = V_0 + (\upsilon + \tfrac{1}{2})\tilde{\nu}_0 hc + J(J+1)\tilde{B}_0 hc$

The midpoint of the 0–0 band corresponds to the forbidden Q branch ($\Delta J = 0$) with $J = 0$ and $\upsilon = 0 \leftarrow 0$.

$$\Delta E_{00} = E_1(0,0) - E_0(0,0) = (V_1 - V_0) + \tfrac{1}{2}\left(\tilde{\nu}_1 - \tilde{\nu}_0\right)hc \quad (1)$$

The midpoint of the 1–1 band corresponds to the forbidden Q branch ($\Delta J = 0$) with $J = 0$ and $\upsilon = 1 \leftarrow 1$.

$$\Delta E_{11} = E_1(1,0) - E_0(1,0) = (V_1 - V_0) + \tfrac{3}{2}(\tilde{\nu}_1 - \tilde{\nu}_0)hc \quad (2)$$

Multiplying eqn 1 by three and subtracting eqn 2 gives

$$3\Delta E_{00} - \Delta E_{11} = 2(V_1 - V_0)$$

$$\begin{aligned} V_1 - V_0 &= \tfrac{1}{2}(3\Delta E_{00} - \Delta E_{11}) \\ &= \tfrac{1}{2}\{3(5.1250) - (5.1409)\} \times 10^{-19}\ \text{J} \\ &= 5.1171 \times 10^{-19}\ \text{J} = \boxed{3.1938\ \text{eV}} \quad (3) \end{aligned}$$

This is the potential energy difference between S_0 and S_1.

Eqns (1) and (3) may be solved for $\tilde{\nu}_1 - \tilde{\nu}_0$.

$$\begin{aligned} \tilde{\nu}_1 - \tilde{\nu}_0 &= 2\{\Delta E_{00} - (V_1 - V_0)\} \\ &= 2\{5.1250 - 5.1171\} \times 10^{-19}\ \text{J}/hc \\ &= 1.5800 \times 10^{-21}\ \text{J} = 0.0098615\ \text{eV} \\ &= \boxed{79.538\ \text{cm}^{-1}} \end{aligned}$$

The $\tilde{\nu}_1$ value can be determined by analyzing the band head data for which $J + 1 \leftarrow J$.

$$\begin{aligned} \Delta E_{10}(J) &= E_1(0,J) - E_0(1,J+1) \\ &= V_1 - V_0 + \tfrac{1}{2}(\tilde{\nu}_1 - 3\tilde{\nu}_0)hc + J(J+1)\tilde{B}_1 hc - (J+1) \times (J+2)\tilde{B}_0 hc \end{aligned}$$

$$\Delta E_{00}(J) = V_1 - V_0 + \tfrac{1}{2}(\tilde{\nu}_1 - \tilde{\nu}_0)hc + J(J+1)\tilde{B}_1 hc - (J+1) \times (J+2)\tilde{B}_0 hc$$

Therefore,

$$\Delta E_{00}(J) - \Delta E_{11}(J) = \tilde{\nu}_0 hc$$

$$\Delta E_{00}(J_{\text{head}}) = \frac{hc}{388.3\ \text{nm}} = 5.1158 \times 10^{-19}\ \text{J}$$

$$\Delta E_{10}(J_{\text{head}}) = \frac{hc}{421.6\ \text{nm}} = 4.7117 \times 10^{-19}\ \text{J}$$

$$\tilde{\nu}_0 = \frac{\Delta E_{00}(J) - \Delta E_{10}(J)}{hc}$$

$$= \frac{(5.1158 - 4.7117) \times 10^{-19}\ \text{J}}{hc}$$

$$= \frac{4.0410 \times 10^{-20}\ \text{J}}{hc} = 0.25222\ \text{eV} = \boxed{2034.3\ \text{cm}^{-1}}$$

$$\tilde{\nu}_1 = \tilde{\nu}_0 + 79.538\ \text{cm}^{-1}$$

$$= (2034.3 + 79.538)\ \text{cm}^{-1} = \boxed{2113.8\ \text{cm}^{-1} = \frac{4.1990 \times 10^{-20}\ \text{J}}{hc}}$$

$$\frac{I_{1\text{-}1}}{I_{0\text{-}0}} \approx \frac{\mathrm{e}^{-E_1(1,0)/kT_{\text{eff}}}}{\mathrm{e}^{-E_1(0,0)/kT_{\text{eff}}}} = \mathrm{e}^{-(E_1(1,0)-E_1(0,0))/kT_{\text{eff}}}$$

$$\approx \mathrm{e}^{-hc\tilde{\nu}_1/kT_{\text{eff}}}$$

$$\ln\left(\frac{I_{1\text{-}1}}{I_{0\text{-}0}}\right) = -\frac{hc\tilde{\nu}_1}{kT_{\text{eff}}}$$

$$T_{\text{eff}} = \frac{hc\tilde{\nu}_1}{k\ln\left(\frac{I_{0\text{-}0}}{I_{1\text{-}1}}\right)} = \frac{4.1990 \times 10^{-20}\ \text{J}}{(1.38066 \times 10^{-23}\ \text{J K}^{-1})\ln(10)} = \boxed{1321\ \text{K}}$$

The relative population of the $\upsilon = 0$ and $\upsilon = 1$ vibrational states is the inverse of the relative intensities of the transitions from those states, hence $\frac{1}{0.1} = \boxed{10}$.

It would seem that with such a high effective temperature more than eight of the rotational levels of the S_1 state should have a significant population, but the spectra of molecules in comets are never as clearly resolved as those obtained in the laboratory and that is most probably why additional rotational structure does not appear in these spectra.

14

Molecular spectroscopy 3: magnetic resonance

Answers to discussion questions

D14.2 Detailed discussions of the origins of the local, neighbouring group and solvent contributions to the shielding constant can be found in Sections 14.5(c), (d), and (e) as well as books on NMR. Here, we will merely summarize the major features.

The local contribution is essentially the contribution of the electrons in the atom that contains the nucleus being observed. It can be expressed as a sum of a diamagnetic and paramagnetic parts, that is $\sigma(\text{local}) = \sigma_d + \sigma_p$. The diamagnetic part arises because the applied field generates a circulation of charge in the ground state of the atom. In turn, the circulating charge generates a magnetic field. The direction of this field can be found through Lenz's law, which states that the induced magnetic field must be opposite in direction to the field producing it. Thus, it shields the nucleus. The diamagnetic contribution is roughly proportional to the electron density on the atom and it is the only contribution for closed-shell free atoms and for distributions of charge that have spherical or cylindrical symmetry. The local paramagnetic contribution is somewhat harder to visualize since there is no simple and basic principle analogous to Lenz's law that can be used to explain the effect. The applied field adds a term to the Hamiltonian of the atom that mixes in excited electronic states into the ground state and any theoretical calculation of the effect requires detailed knowledge of the excited state wavefunctions. It is to be noted that the paramagnetic contribution does not require that the atom or molecule be paramagnetic. It is paramagnetic only in the sense that it results in an induced field in the same direction as the applied field.

The neighbouring group contributions arise in a manner similar to the local contributions. Both diamagnetic and paramagnetic currents are induced in the neighbouring atoms and these currents result in shielding contributions to the nucleus of the atom being observed. However, there are some differences. The magnitude of the effect is much smaller because the induced currents in neighbouring atoms are much farther away. It also depends on the anisotropy of the magnetic susceptibility (see Chapter 19) of the neighbouring group, as shown in eqn 14.23(b). Only anisotropic susceptibilities result in a contribution.

Solvents can influence the local field in many different ways. Detailed theoretical calculations of the effect are difficult due to the complex nature of the solute–solvent interaction. Polar solvent–polar solute interactions are an electric field effect that usually causes deshielding of the solute protons. Solvent magnetic anisotropy can cause shielding or deshielding, for example, for solutes in benzene solution. In addition, there are a variety of specific chemical interactions between solvent and solute that can affect the chemical shift.

D14.4 See Section 14.6(e), Figures 14.24 and 14.25, and *Justification* 14.3 for a detailed explanation of this effect. As demonstrated in the *Justification*, spin–spin splittings between magnetically equivalent nuclei do not appear in the spectrum of groups of equivalent protons. For example, the protons of the methyl group in ethanol become magnetically equivalent because of rapid rotation about the C–C single bond. All three protons have the same time-averaged chemical environment and therefore the same resonance frequencies. If the rotation were slowed or stopped magnetic non-equivalence would re-emerge.

D14.6 Before the application of a pulse the magnetization vector, $\boldsymbol{M}$, points along the direction of the static external magnetic field $\mathcal{B}_0$. There are more α spins than β spins. When we apply a rotating magnetic field $\mathcal{B}_1$ at right angles to the static field, the magnetization vector as seen in the rotating frame begins to precess about the $\mathcal{B}_1$ field with angular frequency $\omega_1 = \gamma\mathcal{B}_1$. The angle through which M rotates is $\theta = \gamma\mathcal{B}_1 t$, where t is the time for which the $\mathcal{B}_1$ pulse is applied. When $t = \pi/2\gamma\mathcal{B}_1$, $\theta = \pi/2 = 90°$, and $\boldsymbol{M}$ has rotated into the xy plane. Now there are equal numbers of α and β spins. A 180° pulse applied for a time $\pi/\gamma\mathcal{B}_1$, rotates $\boldsymbol{M}$ antiparallel to the static field. Now there are more β spins than α spins. A population inversion has occurred.

D14.8 Spin–spin couplings in NMR are due to a polarization mechanism that is transmitted through bonds. The following description applies to the coupling between the protons in an H_X–C–H_Y group, as is typically found in organic compounds. See Figures 14.21–14.23 of the text. On H_X, the Fermi contact interaction causes the spins of its proton and electron to be aligned antiparallel. The spin of the electron from C in the H_X–C bond is then aligned antiparallel to the electron from H_X due to the Pauli exclusion principle. The spin of the C electron in the bond with H_Y is then aligned parallel with the C electron from H_X because of Hund's rule. Finally, the alignment is transmitted through the second bond in the same manner as the first. This progression of alignments (antiparallel × antiparallel × parallel × antiparallel × antiparallel) yields an overall energetically favourable parallel alignment of the two proton nuclear spins, therefore in this case the coupling constant, $^2J_{HH}$ is negative in sign.

The hyperfine structure in the ESR spectrum of an atomic or molecular system is a result of two interactions: an anisotropic dipolar coupling between the net spin of the unpaired electrons and the nuclear spins and also an isotropic coupling due to the Fermi contact interaction. In solution, only the Fermi contact interaction contributes to the splitting as the dipolar contribution averages to zero in a rapidly tumbling system. In the case of π-electron radicals, such as $C_6H_6^-$, no hyperfine interaction between the unpaired electron and the ring protons might have been expected. The protons lie in the nodal plane of the molecular orbital occupied by the unpaired electron, so any hyperfine structure cannot be explained by a simple Fermi contact interaction, which requires an unpaired electron density at the proton. However, an indirect spin polarization mechanism, similar to that used to explain spin–spin couplings in NMR, can account for the existence of proton hyperfine interactions in the ESR spectra of these systems (refer to Figure 14.57 of the text). Because of Hund's rule, the unpaired electron and the first electron in the C–H bond (the one from the C atom), will tend to align parallel to each other. The second electron in the C–H bond (the one from H) will then align antiparallel to the first by the Pauli principle, and finally the Fermi contact interaction will align the proton and electron on H antiparallel. The net result (parallel × antiparallel × antiparallel) is that the spins of the unpaired electron and the proton are aligned parallel and effectively they have detected each other.

Solutions to exercises

E14.1(b) We use eqn 14.9, but with γ [Table 14.2] in place of γ_e.

$$\nu_L = \frac{\gamma\mathcal{B}_0}{2\pi}\,[14.9] = \frac{26.75\times10^7\ \mathrm{T^{-1}\,s^{-1}}\times1.0\ \mathrm{T}}{2\pi} = 4.3\times10^7\ \mathrm{s^{-1}} = \boxed{43\ \mathrm{MHz}}$$

E14.2(b) The relationship between angular velocity and angular displacement is

$$\omega = 2\pi\nu = \frac{\Delta\theta}{t}\ \text{[see any general physics text.]}$$

In this case, ν is the Larmor frequency, ν_L, calculated in Exercise 14.1(b), and $\Delta\theta$ is $\pi/2$. Solving for t we obtain

$$t = \frac{\Delta\theta}{2\pi\nu_L} = \frac{1}{4\nu_L} = \frac{1}{4\times4.3\times10^7\ \mathrm{s^{-1}}} = \boxed{5.8\times10^{-9}\ \mathrm{s}}$$

E14.3(b) For ^{19}F, $g = 5.2567$

$$\nu = \nu_L = \frac{\gamma\mathcal{B}_0}{2\pi}\quad\text{with}\quad\gamma = \frac{g_I\mu_N}{\hbar}$$

Hence, $\nu = \dfrac{g_I\mu_N\mathcal{B}_0}{h} = \dfrac{(5.2567)\times(5.0508\times10^{-27}\ \mathrm{J\,T^{-1}})\times(16.2\ \mathrm{T})}{(6.626\times10^{-34}\ \mathrm{J\,s})}$

$$= 6.49\times10^8\ \mathrm{s^{-1}} = \boxed{649\ \mathrm{MHz}}$$

E14.4(b) The energy separation between the two levels is

$$\Delta E = h\nu,\quad\text{where}\quad \nu = \frac{\gamma\mathcal{B}_0}{2\pi} = \frac{(1.93\times10^7\ \mathrm{T^{-1}\,s^{-1}})\times(15.4\ \mathrm{T})}{2\pi}$$

$$= 4.73\times10^7\ \mathrm{s^{-1}} = \boxed{47.3\ \mathrm{MHz}}$$

E14.5(b) Because the value of the field given in the statement of the exercise is 14 T, we can assume it is a 600-MHz NMR spectrometer. A 600-MHz NMR spectrometer means 600 MHz is the resonance frequency for protons for which the magnetic field is actually 14.1 T, as shown in Exercise 14.3a. In high-field NMR it is the field not the frequency that is fixed.

A ^{14}N nucleus has three energy states in a magnetic field corresponding to $m_I = +1, 0, -1$. But $\Delta E(+1\rightarrow0) = \Delta E(0\rightarrow-1)$

$$\begin{aligned}\Delta E &= E_{m_I'} - E_{m_I} = -\gamma\hbar\mathcal{B}_0m_I' - (-\gamma\hbar\mathcal{B}_0m_I)\\ &= -\gamma\hbar\mathcal{B}_0(m_I' - m_I) = -\gamma\hbar\mathcal{B}_0\Delta m_I\end{aligned}$$

The allowed transitions correspond to $\Delta m_I = \pm1$, hence

$$\Delta E = h\nu = \gamma\hbar\mathcal{B}_0 = g_I\mu_N\mathcal{B}_0 = (0.4036)\times(5.051\times10^{-27}\ \mathrm{J\,T^{-1}})\times(14.1\ \mathrm{T})$$

$$= \boxed{2.88\times10^{-26}\ \mathrm{J}}$$

We assume that the electron g value is equal to the free-electron g value, $g_e = 2.0023$. Then,

$$\Delta E = h\nu = g_e \mu_B \mathcal{B}_0 = (2.0023) \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}}) \times (0.30\ \mathrm{T})$$
$$= \boxed{5.6 \times 10^{-24}\ \mathrm{J}}$$

COMMENT. The energy level separation for the free $\boxed{\text{electron in an EPR spectrometer is far greater}}$ than that of nuclei in an NMR spectrometer, despite the fact that NMR spectrometers normally operate at much higher magnetic fields.

E14.6(b) In all cases the selection rule $\Delta m_I = \pm 1$ is applied, hence (Exercise 14.5b)

$$\mathcal{B}_0 = \frac{h\nu}{g_I \mu_N} = \frac{6.626 \times 10^{-34}\ \mathrm{J\ Hz^{-1}}}{5.0508\ \times 10^{-27}\ \mathrm{J\ T^{-1}}} \times \frac{\nu}{g_I}$$
$$= (1.3119 \times 10^{-7}) \times \frac{\left(\frac{\nu}{\mathrm{Hz}}\right)}{g_I}\mathrm{T}$$
$$= (0.13119) \times \frac{\left(\frac{\nu}{\mathrm{MHz}}\right)}{g_I}\mathrm{T}$$

We can draw up the following table:

	$\mathcal{B}_0/\mathrm{T}$	(a) $^{14}\mathrm{N}$	(b) $^{19}\mathrm{F}$	(c) $^{31}\mathrm{P}$
	g_I	0.40356	5.2567	2.2634
(i)	300 MHz	97.5	7.49	17.4
(ii)	750 MHz	244	18.7	43.5

COMMENT. Magnetic fields above 23 T have not yet been obtained for use in NMR spectrometers. As discussed in the solution to Exercise 14.5b, it is the field, not the frequency, that is fixed in high-field NMR spectrometers. Thus, an NMR spectrometer that is called a 300-MHz spectrometer refers to the resonance frequency for protons and has a magnetic field fixed at 7.05 T.

E14.7(b) The relative population difference for spin $\frac{1}{2}$ nuclei is given by

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\gamma \hbar \mathcal{B}_0}{2kT} = \frac{g_I \mu_N \mathcal{B}_0}{2kT} \quad [\textit{Justification}\ 14.1\ \text{and Exercise 14.7(a)}]$$
$$= \frac{1.405(5.05 \times 10^{-27}\ \mathrm{J\ T^{-1}})\mathcal{B}_0}{2(1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (298\ \mathrm{K})}$$
$$= 8.62 \times 10^{-7}(\mathcal{B}_0/T)$$

(a) For 0.50 T $\quad \dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (0.50) = \boxed{4.3 \times 10^{-7}}$

(b) For 2.5 T $\quad \dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (2.5) = \boxed{2.2 \times 10^{-6}}$

(c) For 15.5 T $\quad \dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (15.5) = \boxed{1.34 \times 10^{-5}}$

E14.8(b) $\mathcal{B}_{\text{nuc}} = -\dfrac{\gamma\hbar\mu_0}{4\pi R^3}(1-3\cos^2\theta)m_I$ [14.28]

We use $m_I = \frac{1}{2}$ and R = 100 pm = 1.00×10^{-10} m and substitute for the constants in the expression. We obtain

$$\mathcal{B}_{\text{nuc}} = \frac{-26.75\times10^{7}\,\text{s}^{-1}\,\text{T}^{-1}\times1.055\times10^{-34}\,\text{J s}\times12.57\times10^{-7}\,\text{T}^2\,\text{J}^{-1}\,\text{m}^3}{8\pi(1.00\times10^{-10}\,\text{m})^3}(1-3\cos^2\theta)$$

$$\mathcal{B}_{\text{nuc}} = -1.411\times10^{-3}\,\text{T}\times(1-3\cos^2\theta)$$

(a) $\theta = 0°$, $\mathcal{B}_{\text{nuc}} = \boxed{2.82\times10^{-3}\,\text{T}}$ (b) $\theta = 90°$, $\mathcal{B}_{\text{nuc}} = \boxed{0}$

E14.9(b) The ground state has

$m_s = +\frac{1}{2} = \alpha$ spin, $m_s = -\frac{1}{2} = \beta$ spin

Hence, with

$$\delta N = N_\beta - N_\alpha$$

$$\frac{\delta N}{N} = \frac{N_\beta - N_\alpha}{N_\beta + N_\alpha} = \frac{N_\beta - N_\beta e^{-\Delta E/kT}}{N_\beta + N_\beta e^{-\Delta E/kT}}$$

$$= \frac{1-e^{-\Delta E/kT}}{1+e^{-\Delta E/kT}} \approx \frac{1-(1-\Delta E/kT)}{1+1} \approx \frac{\Delta E}{2kT} = \frac{g_e\mu_B\mathcal{B}_0}{2kT} \quad [\text{for } \Delta E \ll kT]$$

$$\frac{\delta N}{N} = \frac{2.0023\times9.274\times10^{-24}\,\text{J T}^{-1}\times0.33\,\text{T}}{2\times1.381\times10^{-23}\times T} = \frac{0.2219\,\text{K}}{T}$$

(a) $\dfrac{\delta N}{N} = \dfrac{0.2219\,\text{K}}{298\,\text{K}} = \boxed{7.45\times10^{-4}}$

(b) $\dfrac{\delta N}{N} = \dfrac{0.2219\,\text{K}}{77\,\text{K}} = \boxed{2.88\times10^{-3}}$

Thus, $\dfrac{\delta N}{N} \propto \dfrac{1}{T}$

$$\frac{(\delta N/N)(298\,\text{K})}{(\delta N/N)(77\,\text{K})} = \frac{(77)}{(298)} = \boxed{0.26}$$

This ratio is not dependent on the magnetic field as long as the approximation $\Delta E \ll kT$ holds.

E14.10(b) $\mathcal{B}_{\text{loc}} = (1-\sigma)\mathcal{B}_0$

$$|\Delta\mathcal{B}_{\text{loc}}| = |(\Delta\sigma)|\,\mathcal{B}_0 \approx |[\delta(\text{CH}_3)-\delta(\text{CH}_2)]|\times10^{-6}\mathcal{B}_0$$
$$= |1.16-3.36|\times10^{-6}\mathcal{B}_0 = 2.20\times10^{-6}\mathcal{B}_0$$

(a) $\mathcal{B}_0 = 1.9\,\text{T}$, $|\Delta\mathcal{B}_{\text{loc}}| = (2.20\times10^{-6})\times(1.9\,\text{T}) = \boxed{4.2\times10^{-6}\,\text{T}}$

(b) $\mathcal{B}_0 = 16.5\,\text{T}$, $|\Delta\mathcal{B}_{\text{loc}}| = (2.20\times10^{-6})\times(16.5\,\text{T}) = \boxed{3.63\times10^{-5}\,\text{T}}$

E14.11(b) $\nu - \nu^\circ = \nu^\circ \delta \times 10^{-6}$

$$\begin{aligned}|\Delta\nu| &= (\nu - \nu^\circ)(\mathrm{CH_2}) - (\nu - \nu^\circ)(\mathrm{CH_3}) \\ &= \nu^\circ[\delta(\mathrm{CH_2}) - \delta(\mathrm{CH_3})] \times 10^{-6} \\ &= (3.36 - 1.16) \times 10^{-6}\nu^\circ = 2.20 \times 10^{-6}\,\nu^\circ\end{aligned}$$

(a) $\nu^\circ = 350\ \mathrm{MHz}$ $|\Delta\nu| = (2.20 \times 10^{-6}) \times (350\ \mathrm{MHz}) = 770\ \mathrm{Hz}$ [Figure. 14.1]

(b) $\nu^\circ = 650\ \mathrm{MHz}$ $|\Delta\nu| = (2.20 \times 10^{-6}) \times (650\ \mathrm{MHz}) = 1.43\ \mathrm{kHz}$

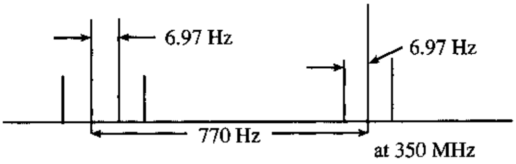


Figure 14.1

At 650 MHz, the spin–spin splitting remains the same at 6.97 Hz, but as $\Delta\nu$ has increased to 1.43 kHz, the splitting appears narrower on the δ scale.

E14.12(b) See Section 14.6(b), Example 14.1 and Figures 14.16–14.19 for the approach to the solution to this exercise. Also, see Example 14.2 and Figures 14.55 and 14.56. That latter example and those figures are applied specifically to EPR spectra, but the process of determining the intensity pattern in the fine structure of an NMR spectrum is the same. See the table below for the version of Pascal's triangle for up to three spin-$\frac{5}{2}$ nuclei. Each number in the table is the sum of the six ($I = \frac{5}{2}$, $2I + 1 = 6$) numbers above it (three to the right and three to the left).

															1															
										1		1		1		1		1		1										
					1		2		3		4		5		6		5		4		3		2		1					
1		3		6		10		15		21		25		27		27		25		21		15		10		6		3		1

E14.13(b) $\tau \approx \dfrac{\sqrt{2}}{\pi\Delta\nu}$ [14.29, with $\delta\nu$ written as $\Delta\nu$]

$\Delta\nu = \nu^\circ(\delta' - \delta) \times 10^{-6}$ [Exercise 14.13a]

Then, $$\tau \approx \frac{\sqrt{2}}{\pi\nu_0(\delta' - \delta) \times 10^{-6}} \approx \frac{\sqrt{2}}{(\pi) \times (350 \times 10^6\ \mathrm{Hz}) \times (5.5 - 4.2) \times 10^{-6}} \approx 9.9 \times 10^{-4}\ \mathrm{s}$$

Therefore, the signals merge when the lifetime of each isomer is less than about $\boxed{0.99\ \mathrm{ms}}$, corresponding to a conversion rate of about $\boxed{1.0 \times 10^3\ \mathrm{s^{-1}}}$.

E14.14(b) $\nu = \dfrac{g_I \mu_N \mathcal{B}_0}{h}$ [solution to Exercise 14.3(a)]

Hence, $\dfrac{\nu(^{31}\mathrm{P})}{\nu(^{1}\mathrm{H})} = \dfrac{g(^{31}\mathrm{P})}{g(^{1}\mathrm{H})}$

or $\nu(^{31}\text{P}) = \dfrac{2.2634}{5.5857} \times 500\ \text{MHz} = \boxed{203\ \text{MHz}}$

The proton resonance consists of two lines $(2 \times \frac{1}{2} + 1)$ and the ^{31}P resonance of five lines $[2 \times (4 \times \frac{1}{2}) + 1]$. The intensities are in the ratio 1:4:6:4:1 (Pascal's triangle for four equivalent spin $\frac{1}{2}$ nuclei, Section 14.6). The lines are spaced $\dfrac{5.5857}{2.2634} = 2.47$ times greater in the phosphorus region than the proton region. The spectrum is sketched in Figure 14.2.

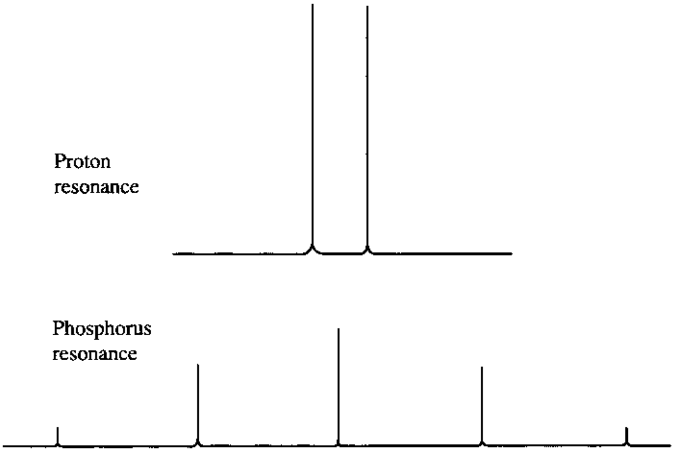


Figure 14.2

E14.15(b) Look first at A and M, since they have the largest splitting. The A resonance will be split into a widely spaced triplet (by the two M protons); each peak of that triplet will be split into a less widely spaced sextet (by the five X protons). The M resonance will be split into a widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced sextet (by the five X protons). The X resonance will be split into a less widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced triplet (by the two M protons) (see Figure 14.3). Only the splitting of the central peak of Figure 14.3(a) is shown in Figure 14.3(b).

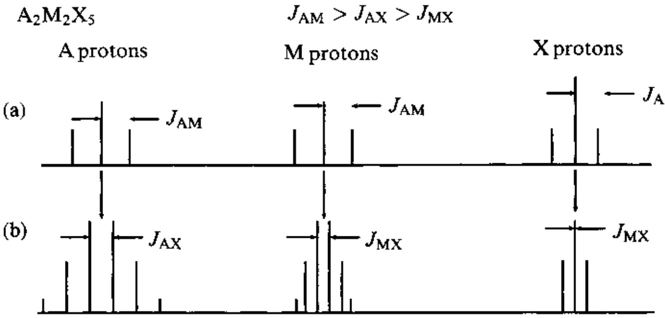


Figure 14.3

E14.16(b) (a) Since all J_{HF} are equal in this molecule (the CH_2 group is perpendicular to the CF_2 group), the H and F nuclei are both chemically and magnetically equivalent.

(b) Rapid rotation of the PH_3 groups about the Mo–P axes makes the P and H nuclei chemically and magnetically equivalent in both the *cis* and *trans* forms.

E14.17(b) The effective transverse relaxation time is given by

$$T_2^* = \frac{1}{\pi\Delta\nu_{1/2}}\,[14.34] = \frac{1}{\pi \times 12\ \mathrm{s}^{-1}} = \boxed{0.027\ \mathrm{s}}$$

E14.18(b) The maximum enhancement is given by

$$\eta = \frac{\gamma_{^1\mathrm{H}}}{2\times\gamma_{^{19}\mathrm{F}}}\,[14.37] = \frac{26.752\times10^{7}\ \mathrm{T^{-1}\,s^{-1}}}{2\times25.177\times10^{7}\ \mathrm{T^{-1}\,s^{-1}}}\,[\text{Table 14.2}] = \boxed{0.5312}$$

E14.19(b) Precession in the rotating frame follows

$$\nu_\mathrm{L} = \frac{\gamma\mathcal{B}_1}{2\pi} \quad \text{or} \quad \omega_1 = \gamma\mathcal{B}_1$$

Since ω is an angular frequency, the angle through which the magnetization vector rotates is

$$\theta = \gamma\mathcal{B}_1 t = \frac{g_I\mu_\mathrm{N}}{\hbar}\mathcal{B}_1 t$$

$$\text{So } \mathcal{B}_1 = \frac{\theta\hbar}{g_I\mu_\mathrm{N}t} = \frac{(\pi)\times(1.0546\times10^{-34}\ \mathrm{J\,s})}{(5.586)\times(5.0508\times10^{-27}\ \mathrm{J\,T^{-1}})\times(12.5\times10^{-6}\ \mathrm{s})} = \boxed{9.40\times10^{-4}\ \mathrm{T}}$$

a 90° pulse requires $\frac{1}{2}\times12.5\ \mu\mathrm{s} = \boxed{6.25\ \mu\mathrm{s}}$.

E14.20(b)

$$\mathcal{B}_0 = \frac{h\nu}{g_\mathrm{e}\mu_\mathrm{B}} = \frac{hc}{g_\mathrm{e}\mu_\mathrm{B}\lambda} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})\times(2.998\times10^{8}\ \mathrm{m\,s^{-1}})}{(2.0023)\times(9.274\times10^{-24}\ \mathrm{J\,T^{-1}})\times(8\times10^{-3}\ \mathrm{m})} = \boxed{1.\bar{3}\ \mathrm{T}}$$

E14.21(b) The g factor is given by

$$g = \frac{h\nu}{\mu_\mathrm{B}\mathcal{B}_0};\quad \frac{h}{\mu_\mathrm{B}} = \frac{6.62608\times10^{-34}\ \mathrm{J\,s}}{9.2740\times10^{-24}\ \mathrm{J\,T^{-1}}} = 7.1448\times10^{-11}\ \mathrm{T\,Hz^{-1}} = 71.448\ \mathrm{mT\,GHz^{-1}}$$

$$g = \frac{71.448\ \mathrm{mT\,GHz^{-1}}\times9.2482\ \mathrm{GHz}}{330.02\ \mathrm{mT}} = \boxed{2.0022}$$

E14.22(b) The hyperfine coupling constant for each proton is $\boxed{2.2\ \mathrm{mT}}$, the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_\mathrm{B}\mathcal{B}_0} = \frac{(71.448\ \mathrm{mT\,GHz^{-1}})\times(9.332\ \mathrm{GHz})}{334.7\ \mathrm{mT}} = \boxed{1.992}$$

E14.23(b) If the spectrometer has sufficient resolution, it will see a signal split into eight equal parts at ±1.445, ±1.435, ±1.055 mT from the centre, namely

$$\boxed{\text{328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625 and 336.735 mT}}$$

If the spectrometer can only resolve to the nearest 0.1 mT, then the spectrum will appear as a sextet with intensity ratios of 1:1:2:2:1:1. The four central peaks of the more highly resolved spectrum would be the two central peaks of the less-resolved spectrum.

E14.24(b) (a) If the CH_2 protons have the larger splitting there will be a triplet (1:2:1) of quartets (1:3:3:1). Altogether, there will be 12 lines with relative intensities 1(4 lines), 2(2 lines), 3(4 lines), and 6(2 lines). Their positions in the spectrum will be determined by the magnitudes of the two proton splittings, which are not given.

(b) If the CD_2 deuterons have the larger splitting there will be a quintet (1:2:3:2:1) of septets (1:3:6:7:6:3:1). Altogether, there will be 35 lines with relative intensities 1(4 lines), 2(4 lines), 3(6 lines), 6(8 lines), 7(2 lines), 9(2 lines), 12(4 lines), 14(2 lines), 18(2 lines), and 21(1 line). Their positions in the spectrum will determined by the magnitude of the two deuteron splittings, which are not given.

E14.25(b) The g value is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}_0}, \quad \text{so} \quad \mathcal{B}_0 = \frac{h\nu}{\mu_B g}, \quad \frac{h}{\mu_B} = 71.448 \text{ mT GHz}^{-1}$$

$$\text{(a)} \quad \mathcal{B}_0 = \frac{(71.448 \text{ mT GHz}^{-1}) \times (9.312 \text{ GHz})}{2.0024} = \boxed{332.3 \text{ mT}}$$

$$\text{(b)} \quad \mathcal{B}_0 = \frac{(71.448 \text{ mT GHz}^{-1}) \times (33.88 \text{ GHz})}{2.0024} = \boxed{1209 \text{ mT}}$$

E14.26(b) Two nuclei of spin $\boxed{I = 1}$ give five lines in the intensity ratio 1:2:3:2:1 (Figure 14.4).

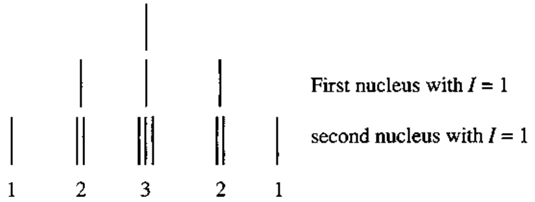


Figure 14.4

E14.27(b) The X nucleus produces four lines of equal intensity. Three H nuclei split each into a 1:3:3:1 quartet. The three D nuclei split each line into a septet with relative intensities 1:3:6:7:6:3:1 (see Exercise 14.24a and Figure 14.5).

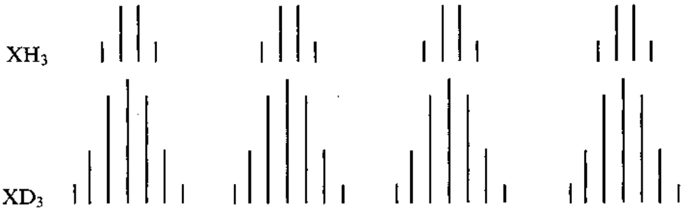


Figure 14.5

E14.28(b) We assume that the condition for the coalescence of two EPR lines is the same as the condition for the coalescence of two NMR lines, that is the coalescence time is given by $\tau = \frac{\sqrt{2}}{\pi\delta\nu}$ [14.29]. Then, we need to calculate $\delta\nu$ corresponding to the frequency difference of the two EPR resonances, $g_{\parallel}$ and $g_{\perp}$. We have $h\nu = g\mu_B\mathcal{B}_0$ [14.39]. Solve for ν.

$$\nu = \frac{\mu_B}{h}\mathcal{B}_0 g, \text{ and then}$$

$$\delta\nu = \frac{\mu_B}{h}\mathcal{B}_0(\delta g) = \frac{9.274\times10^{-24}\,\text{J T}^{-1}}{6.626\times10^{-34}\,\text{J s}}\times1.0\,\text{T}\times(2.023-2.022) = 1.40\times10^{7}\,\text{s}^{-1}$$

$$\tau = \frac{\sqrt{2}}{\pi\delta\nu} = \frac{\sqrt{2}}{\pi\times1.4\times10^{7}\,\text{s}^{-1}} = 3.22\times10^{-8}\,\text{s}$$

The tumbling rate is the inverse of this time, $\boxed{3.1\times10^{7}\,\text{s}^{-1}}$.

Solutions to problems

Solutions to numerical problems

P14.2 When $\nu = 60$ MHz

$$\tau_J = \frac{\sqrt{2}}{\pi\delta\nu} \approx \frac{\sqrt{2}}{\pi\Delta\nu} = \frac{\sqrt{2}}{\pi\times((5.2-4.0)\times10^{-6})\times(60\times10^{6}\,\text{Hz})}$$

≈ 6.25 ms, corresponding to a jump rate of 160 s^{-1}.

When $\nu = 300$ MHz

$$\tau_J = \frac{\sqrt{2}}{\pi\delta\nu} \approx \frac{\sqrt{2}}{\pi\Delta\nu} = \frac{\sqrt{2}}{\pi\times((5.2-4.0)\times10^{-6})\times(300\times10^{6}\,\text{Hz})}$$

≈ 1.25 ms, corresponding to a jump rate of $8.0\times10^{2}\,\text{s}^{-1}$.

Assume an Arrhenius-like jumping process (Chapter 21)

$$\text{rate} \propto e^{-E_a/RT}$$

$$\text{Then, } \ln\left[\frac{\text{rate}(T')}{\text{rate}(T)}\right] = \frac{-E_a}{R}\left(\frac{1}{T'}-\frac{1}{T}\right)$$

$$\text{and therefore } E_a = \frac{R\ln(r'/r)}{\frac{1}{T}-\frac{1}{T'}} = \frac{8.314\,\text{J K}^{-1}\text{mol}^{-1}\times\ln\frac{800}{160}}{\frac{1}{280\,\text{K}}-\frac{1}{300\,\text{K}}} = \boxed{56\,\text{kJ mol}^{-1}}$$

P14.4 The FID signals from the three nuclei are all of the form of eqn 14.30, which we will write as $F(t) = \sum_j S_{0j}\cos(2\pi\nu_{Lj}t)e^{-t/T_{2j}}$. For simplicity, we will assume that all T_2 values are the same at 1.0 s and that the maximum signal intensity S_{0j} is the same for each nucleus. No information is given in the problem statement about the number of nuclei with the specific values of δ given, so again for simplicity we will assume only one nucleus corresponds to each value of δ. The total FID can then be expressed as

$$F(t) = S_0\sum_j\cos(2\pi\nu_{Lj}t)e^{-t/T_2}$$

The solution is contained in the following MathCad® worksheet and Figure 14.6.

Definitions: $\mathrm{MHz} := 10^6 \cdot \mathrm{Hz}$ $\quad N := 2^{12}$

$m := 0, 1 .. N-1$

Time domain: $t_{max} := 10 \cdot s$ $\quad t_m := \frac{m}{N} \cdot t_{max}$

Relaxation time: $T_2 := 1 \cdot s$

Chemical shifts: $\delta_1 := 3.2 \quad \delta_2 := 4.1 \quad \delta_3 := 5.0$

Spectrometer frequency: $\nu_0 := 800 \cdot \mathrm{MH_z}$

Relative intensities: $S_1 := 1 \quad S_2 := 1 \quad S_3 := 1$

Larmor frequencies: $\nu_1 := \left(1 + \frac{\delta_1}{10^6}\right) \cdot \nu_0 \quad \nu_2 := \left(1 + \frac{\delta_2}{10^6}\right) \cdot \nu_0 \quad \nu_3 := \left(1 + \frac{\delta_3}{10^6}\right) \cdot \nu_0$

FID of signal 1: $F_{1_m} := S_1 \cdot \cos(2 \cdot \pi \cdot \nu_1 \cdot t_m) \cdot e^{\frac{-t_m}{T_2}}$

FID of signal 2: $F_{2_m} := S_2 \cdot \cos(2 \cdot \pi \cdot \nu_2 \cdot t_m) \cdot e^{\frac{-t_m}{T_2}}$

FID of signal 3: $F_{3_m} := S_3 \cdot \cos(2 \cdot \pi \cdot \nu_3 \cdot t_m) \cdot e^{\frac{-t_m}{T_2}}$

Total FID signal: $F := F_1 + F_2 + F_3$

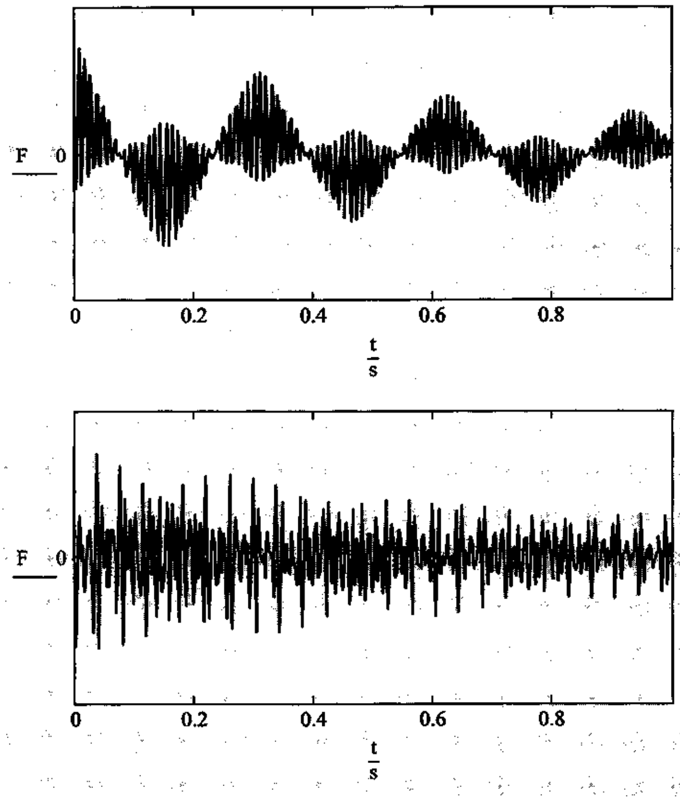


Figure 14.6(a) & (b)

The FIDs of the signal from this compound with the values of the chemical shifts given in this problem are just a jumble of lines with intensities decreasing with time; the FIDs themselves contain very little direct information about the compound. The desired information is extracted by Fourier transformation of the FIDs from the time domain to the frequency domain. Increasing the frequency of the spectrometer from 200 MHz to 800 MHz has no effect upon the chemical shift expressed as δ values, but does increase the chemical shift expressed as $(\nu_L - \nu_0)$ values and that is the main reason for building spectrometers operating at higher and higher frequencies. Increasing the frequency (and hence the field) allows for greater resolution of spin–spin splittings in the spectrum as the chemical shift $(\nu_L - \nu_0)$ increases. That would not be obvious in this example because no information is given about spin–spin splittings. As an example of this problem in a real substance, ethanol, where spin–spin splittings occur, examine Figures 14.34 and 14.6 of the text.

P14.6 It seems reasonable to assume that only staggered conformations can occur, therefore the equilibria are as shown in Figure 14.7.

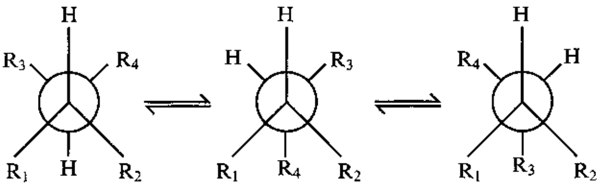


Figure 14.7

When $R_3 = R_4 = H$, all three of the above conformations occur with equal probability:

$${}^3J_{HH}\text{ (methyl)} = \tfrac{1}{3}({}^3J_t + 2\,{}^3J_g) \quad [t = \textit{trans},\ g = \text{gauche};\ CHR_3R_4 = \text{methyl}]$$

The first conformation in the figure is *trans*, the second two are gauche.

Additional methyl groups will avoid being staggered between both R_1 and R_2, therefore

$${}^3J_{HH}\text{(ethyl)} = \tfrac{1}{2}({}^3J_t + {}^3J_g) \quad [R_4 = H, R_3 = CH_3]$$

$${}^3J_{HH}\text{(isopropyl)} = {}^3J_t \quad [R_3 = R_4 = CH_3]$$

We then have three simultaneous equations in two unknowns J_t and J_g:

$$\tfrac{1}{3}({}^3J_t + 2\,{}^3J_g) = 7.3\text{ Hz} \quad (1)$$

$$\tfrac{1}{2}({}^3J_t + {}^3J_g) = 8.0\text{ Hz} \quad (2)$$

$${}^3J_t = 11.2\text{ Hz}$$

The two unknowns are overdetermined. The first two equations yield ${}^3J_t = 10.1$, ${}^3J_g = 5.9$. However, if we assume that ${}^3J_t = 11.2$ as measured directly in the isopropyl case then ${}^3J_g = 5.4$ (eqn 1) or 4.8 (eqn 2), with an average value of 5.1.

Using the original form of the Karplus equation

$${}^3J_t = A\cos^2(180°) + B = 11.2$$

$${}^3J_g = A\cos^2(60°) + B = 5.1$$

or

$$11.2 = A + B$$

$$5.1 = 0.25\,A + B$$

These simultaneous equations yield $A = 6.8$ Hz and $B = 4.8$ Hz. With these values of A and B, the original form of the Karplus equation fits the data exactly (at least to within the error in the values of ${}^3J_t$ and ${}^3J_g$ and in the measured values reported).

From the form of the Karplus equation in the text [14.27] we see that those values of A, B, and C cannot be determined from the data given, as there are three constants to be determined from only two values of J. However, if we use the values of A, B, and C given in the text, then

$$J_t = 7\text{ Hz} + 1\text{ Hz}(\cos 180°) + 5\text{ Hz}(\cos 360°) = 11\text{ Hz}$$

$$J_g = 7\text{ Hz} + 1\text{ Hz}(\cos 60°) + 5\text{ Hz}(\cos 120°) = 5\text{ Hz}$$

The agreement with the modern form of the Karplus equation is excellent, but not better than the original version. $\boxed{\text{Both fit the data equally well,}}$ but the modern version is preferred as it is more generally applicable.

P14.8 The proton COSY spectrum of 1-nitropropane shows that (a) the C_a–H resonance with $\delta = 4.3$ shares a cross-peak with the C_b–H resonance at $\delta = 2.1$ and (b) the C_b–H resonance with $\delta = 2.1$ shares a cross-peak with the C_c–H resonance at $\delta = 1.1$. Off-diagonal peaks indicate coupling between Hs on various carbons. Thus peaks at (4,2) and (2,4) indicate that the Hs on the adjacent CH_2 units are coupled. The peaks at (1,2) and (2,1) indicate that the Hs on CH_3 and central CH_2 units are coupled. See Figure 14.8.

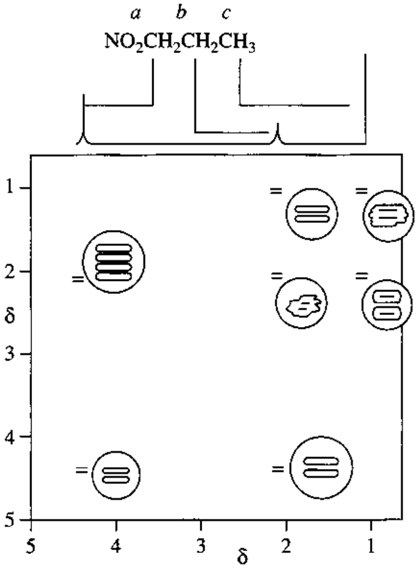


Figure 14.8

P14.10

$$g = \frac{h\nu}{\mu_B \mathcal{B}_0}\,[14.39] = \frac{(7.14478\times 10^{-11}\,\mathrm{T})\times(\nu/\mathrm{Hz})}{\mathcal{B}_0}$$

$$= \frac{(7.14478\times 10^{-11}\,\mathrm{T})\times(9.302\times 10^{9})}{\mathcal{B}_0}$$

$$= \frac{0.6646\bar{1}}{\mathcal{B}_0/T}$$

$$g_{\parallel} = \frac{0.6646\bar{1}}{0.33364} = \boxed{1.992} \quad g_{\perp} = \frac{0.6646\bar{1}}{0.33194} = \boxed{2.002}$$

P14.12 Construct the spectrum by taking into account first the two equivalent ^{14}N splitting (producing a $\boxed{1:2:3:2:1 \text{ quintet}}$) and then the splitting of each of these lines into a $\boxed{1:4:6:4:1 \text{ quintet}}$ by the four equivalent protons. The resulting 25-line spectrum is shown in Figure 14.9. Note that Pascal's triangle does not apply to the intensities of the quintet due to ^{14}N, but does apply to the quintet due to the protons.

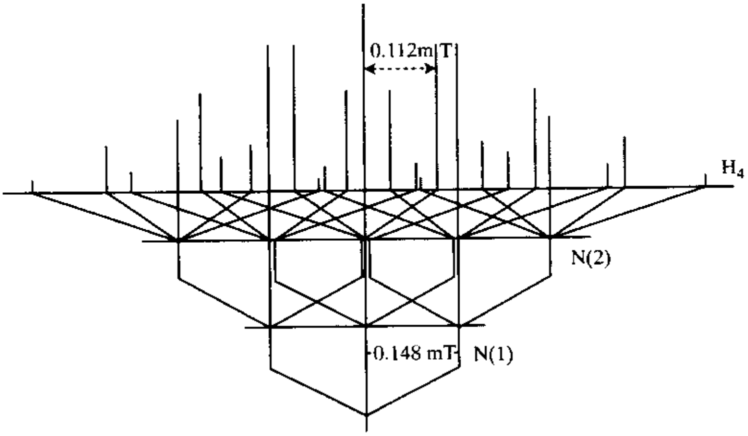
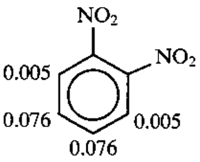


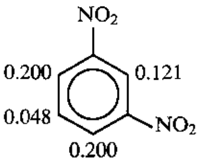
Figure 14.9

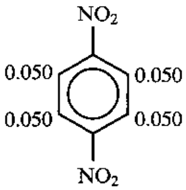
P14.14 For $C_6H_6^-$, $a = Q\rho$ with $Q = 2.25$ mT [14.42]. If we assume that the value of Q does not change from this value (a good assumption in view of the similarity of the anions), we may write

$$\rho = \frac{a}{Q} = \frac{a}{2.25\,\mathrm{mT}}$$

Hence, we can construct the following maps







Solutions to theoretical problems

P14.16 (a) The table displays experimental ^{13}C chemical shifts and computed* atomic charges on the carbon atom *para* to a number of substituents in substituted benzenes. Two sets of charges are shown, one derived by fitting the electrostatic potential and the other by Mulliken population analysis (see Figure 14.10).

Substituent	OH	CH_3	H	CF_3	CN	NO_2
δ	130.1	128.4	128.5	128.9	129.1	129.4
Electrostatic charge/e	−0.1305	−0.1273	−0.0757	−0.0227	−0.0152	−0.0541
Mulliken charge/e	−0.1175	−0.1089	−0.1021	−0.0665	−0.0805	−0.0392

*Semi-empirical, PM3 level, PC Spartan Pro™

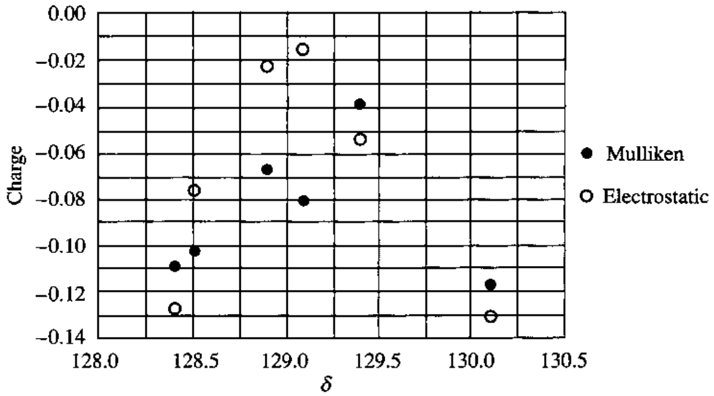


Figure 14.10

(b) Neither set of charges correlates well to the chemical shifts. If one removes phenol from the data set, a correlation would be apparent, particularly for the Mulliken charges.

(c) The diamagnetic local contribution to shielding is roughly proportional to the electron density on the atom. The extent to which the *para* carbon atom is affected by electron-donating or -withdrawing groups on the other side of the benzene ring is reflected in the net charge on the atom. If the diamagnetic local contribution dominated, then the more positive the atom, the greater the deshielding and the greater the chemical shift δ would be. That no such correlation is observed leads to several possible hypotheses, for example the diamagnetic local contribution is not the dominant contribution in these molecules (or not in all of these molecules) or the computation is not sufficiently accurate to provide meaningful atomic charges.

P14.18

$$\langle \mathcal{B}_{\text{nucl}} \rangle = \frac{-g_I \mu_N \mu_0 m_I}{4\pi R^3} \frac{\int_0^{\theta_{\max}} (1-3\cos^2\theta)\sin\theta \, d\theta}{\int_0^{\theta_{\max}} \sin\theta \, d\theta}$$

The denominator is the normalization constant, and ensures that the total probability of being between 0 and $\theta_{\max}$ is 1.

$$= \frac{-g_I\mu_N\mu_0 m_I}{4\pi R^3} \frac{\int_1^{x_{\max}} (1-3x^2)\mathrm{d}x}{\int_1^{x_{\max}} \mathrm{d}x} [x_{\max} = \cos\theta_{\max}]$$

$$= \frac{-g_I\mu_N\mu_0 m_I}{4\pi R^3} \times \frac{x_{\max}(1-x_{\max}^2)}{x_{\max}-1}$$

$$= \boxed{\frac{-g_I\mu_N\mu_0 m_I}{4\pi R^3}(\cos^2\theta_{\max} + \cos\theta_{\max})}$$

If, $\theta_{\max} = \pi$(complete rotation), $\cos\theta_{\max} = -1$ and $\langle \mathcal{B}_{\text{nucl}} \rangle = 0$

If, $\theta_{\max} = 30°$, $\cos^2\theta_{\max} + \cos\theta_{\max} = 1.616$, and

$$\langle \mathcal{B}_{\text{nucl}} \rangle = \frac{(5.5857)\times(5.0508\times10^{-27}\ \text{J T}^{-1})\times(4\pi\times10^{-7}\ \text{T}^2\ \text{J}^{-1}\ \text{m}^3)\times(1.616)}{(4\pi)\times(1.58\times10^{-10}\ \text{m})^3\times(2)}$$

$$= \boxed{0.58\ \text{mT}}$$

P14.20 We have seen (Problem 14.19) that, if $S(t) \propto \cos\omega_0 t$, then $I(\omega) \propto \frac{1}{[1+(\omega_0-\omega)^2\tau^2]}$, which peaks at $\omega \approx \omega_0$. Therefore, if

$$S(t) \propto a\cos\omega_1 t + b\cos\omega_2 t$$

we can anticipate that

$$I(\omega) \propto \frac{a}{1+(\omega_1-\omega)^2\tau^2} + \frac{b}{1+(\omega_2-\omega)^2\tau^2}$$

and explicit calculation shows this to be so, therefore $I(\omega)$ consists of two absorption lines, one peaking at $\omega \approx \omega_1$ and the other at $\omega \approx \omega_2$.

Solution to applications

P14.22 Methionine-105 is in the vicinity of both tryptophan-28 and tyrosine-23 but the latter two residues are not in the vicinity of each other. The methionine residue may lie between them, as represented in Figure 14.11.

P14.24 The desired result is the linear equation:

$[\text{I}]_0 = \frac{[E]_0\Delta v}{\delta v} - K$, [**Note:** The intercept turns out to be $-K$, not K as K is defined in the problem statement.]

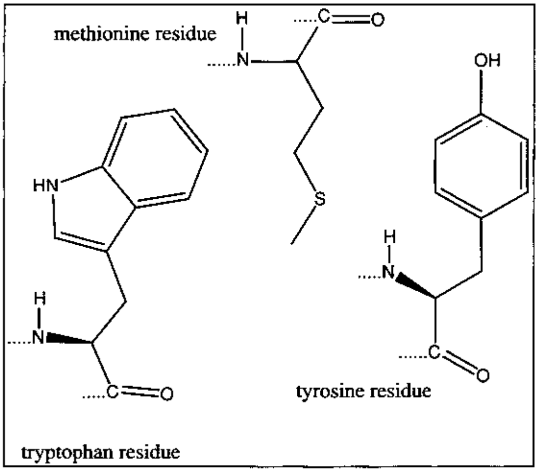


Figure 14.11

Our first task is to express quantities in terms of $[\mathrm{I}]_0$, $[\mathrm{E}]_0$, $\Delta\nu$, $\delta\nu$, and K, eliminating terms such as [I], [EI], [E], ν_I, ν_EI, and ν. [**Note:** symbolic mathematical software is helpful here.] Begin with ν:

$$\nu = \frac{[\mathrm{I}]}{[\mathrm{I}]+[\mathrm{EI}]}\nu_\mathrm{I} + \frac{[\mathrm{EI}]}{[\mathrm{I}]+[\mathrm{EI}]}\nu_\mathrm{EI} = \frac{[\mathrm{I}]_0-[\mathrm{EI}]}{[\mathrm{I}]_0}\nu_\mathrm{I} + \frac{[\mathrm{EI}]}{[\mathrm{I}]_0}\nu_\mathrm{EI},$$

where we have used the fact that total I (i.e. free I plus bound I) is the same as initial I. Solve this so it must also be much greater than [EI]:

$$[\mathrm{EI}] = \frac{[\mathrm{I}]_0(\nu-\nu_\mathrm{I})}{\nu_\mathrm{EI}-\nu_\mathrm{I}} = \frac{[\mathrm{I}]_0\delta\nu}{\Delta\nu},$$

where in the second equality we notice that the frequency differences that appear are the ones defined in the problem. Now, take the equilibrium constant:

$$K = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]} = \frac{([\mathrm{E}]_0-[\mathrm{EI}])([\mathrm{I}]_0-[\mathrm{EI}])}{[\mathrm{EI}]} \approx \frac{([\mathrm{E}]_0-[\mathrm{EI}])[\mathrm{I}]_0}{[\mathrm{EI}]}$$

We have used the fact that total I is much greater than total E (from the condition that $[\mathrm{I}]_0 \gg [\mathrm{E}]_0$), so it must also be much greater than [EI], even if all E binds I. Now solve this for $[\mathrm{E}]_0$:

$$[\mathrm{E}]_0 = \frac{K+[\mathrm{I}]_0}{[\mathrm{I}]_0}[\mathrm{EI}] = \left(\frac{K+[\mathrm{I}]_0}{[\mathrm{I}]_0}\right)\left(\frac{[\mathrm{I}]_0\delta\nu}{\Delta\nu}\right) = \frac{(K+[\mathrm{I}]_0)\delta\nu}{\Delta\nu}$$

The expression contains the desired terms and only those terms. Solving for $[\mathrm{I}]_0$ yields:

$$\boxed{[\mathrm{I}]_0 = \frac{[\mathrm{E}]_0\Delta\nu}{\delta\nu} - K}$$

which would result in a straight line with slope $[\mathrm{E}]_0\Delta\nu$ and y-intercept $-K$ if one plots $[\mathrm{I}]_0$ against $1/\delta\nu$.

P14.26 When spin label molecules approach to within 800 pm, orbital overlap of the unpaired electrons and dipolar interactions between magnetic moments cause an exchange coupling interaction between the spins. The electron exchange process occurs at a rate that increases as concentration increases. Thus, the process has a lifetime that is too long at low concentrations to affect the 'pure' ESR signal. As the concentration increases, the linewidths increase until the triplet coalesces into a broad singlet. Further increase of the concentration decreases the exchange lifetime and therefore the linewidth of the singlet. (See Figure 14.12.)

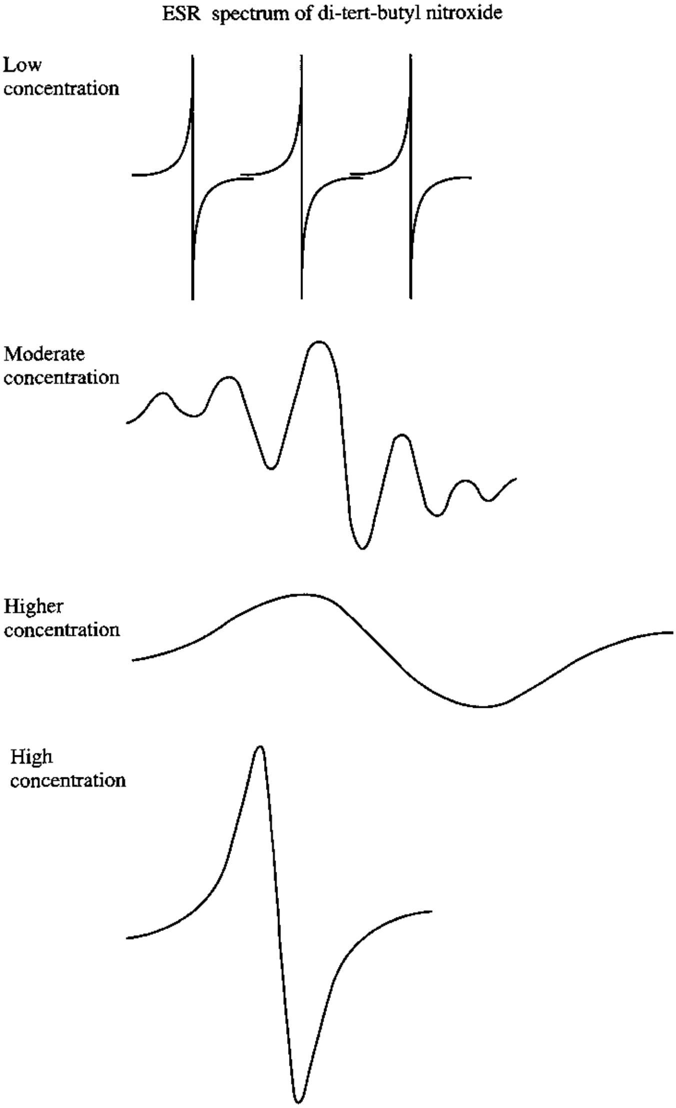


Figure 14.12

When spin labels within biological membranes are highly mobile, they may approach closely and the exchange interaction may provide the ESR spectra with information that mimics the moderate and high concentration signals above.

P14.28 Assume that the radius of the disk is 1 unit. The volume of each slice is proportional to (length of slice × δ_x) (Figure 14.13).

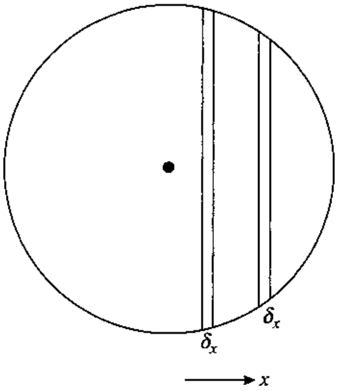


Figure 14.13(a)

length of slice at $x = 2 \sin \theta$

$x = \cos \theta$

$\theta = \arccos x$

ranges from −1 to +1

length of slice at $x = 2 \sin(\arccos x)$

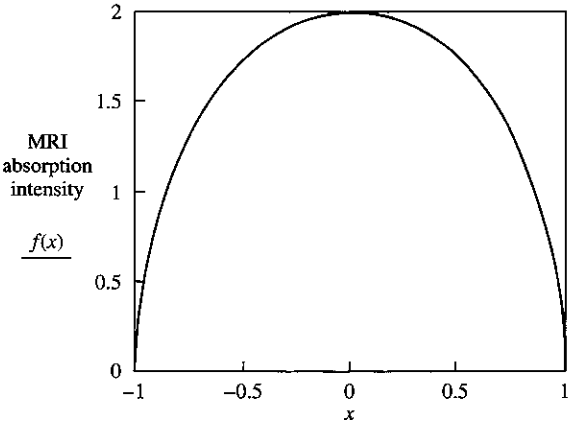


Figure 14.13(b)

Plot $f(x) = 2 \sin(\arccos x)$ against x between the limits −1 and +1. The plot is shown in Figure 14.13(b). The volume at each value of x is proportional to $f(x)$ and the intensity of the MRI signal is proportional to the volume, so Figure 14.13(b) represents the absorption intensity for the MRI image of the disk.

15

Statistical thermodynamics 1: the concepts

Answers to discussion questions

D15.2 See Figures 15.8 and 15.10, the *Brief Illustration* in Section 15.3(a), and *Self-test* 15.6 for details. If the levels are non-degenerate, then both quantities increase from zero to a limiting value in a roughly sigmoidal shape. At very low temperatures, only the lower energy level is accessible, resulting in a highly ordered system at the energy of the lower level. At very high temperatures, the states are occupied practically equally, giving a highly disordered system whose mean energy is halfway between the two levels.

D15.4 Because this chapter focuses on the application of statistics to the distribution of physical states in systems that contain a large number of atoms or molecules, we begin with a statistical answer: the thermodynamic temperature is the one quantity that determines the most probable populations of those states in systems at thermal equilibrium, as explained in Section 15.1(b). As a consequence, the temperature provides a necessary condition for thermal equilibrium; a system is at thermal equilibrium only if all of its subsystems have the same temperature. Note that this is not a circular definition of temperature, for thermal equilibrium is not defined by uniformity of temperature: systems whose subsystems can exchange energy tend toward thermal equilibrium. In this context, subsystems can be different materials placed in contact (such as a block of copper in a beaker of water) or can be more abstract (such as rotational and vibrational modes of motion).

Finally, the equipartition theorem allows us to connect the temperature of statistical thermodynamics to the empirical concept of temperature developed long beforehand. Temperature is a measure of the intensity of thermal energy, directly proportional to the mean energy for each quadratic contribution to the energy (provided that the temperature is sufficiently high).

D15.6 An ensemble is a set of a large number of imaginary replications of the actual system. These replications are identical in some respects, but not in all respects. For example, in the canonical ensemble, all replications have the same number of particles, the same volume, and the same temperature, but need not have the same energy. Ensembles are useful in statistical thermodynamics because it is mathematically more tractable to perform an ensemble average to determine (time-averaged) thermodynamic properties than it is to perform an average over time to determine these properties. Recall that macroscopic thermodynamic properties are averages over the time-dependent properties of the particles that compose the macroscopic system. In fact, it is taken as a fundamental principle of statistical thermodynamics that the (sufficiently long) time average of every physical observable is equal to its ensemble average.

Solutions to exercises

E15.1(b) The weight is given by

$$\mathcal{W}=\frac{N!}{N_0!N_1!N_2!\cdots}=\frac{21!}{6!0!5!0!4!0!3!0!2!0!0!1!}=\boxed{2.04\times10^{12}}$$

E15.2(b) Apply eqn 15.7 to each level. For two non-degenerate levels,

$$\frac{N_2}{N_1}=\frac{\mathrm{e}^{-\beta\varepsilon_2}}{q}\times\frac{q}{\mathrm{e}^{-\beta\varepsilon_1}}=\mathrm{e}^{-\beta(\varepsilon_2-\varepsilon_1)}=\mathrm{e}^{-\beta\Delta\varepsilon}=\mathrm{e}^{-\Delta\varepsilon/kT}$$

Hence, as T approaches 0, the exponent becomes infinitely large and negative:

$$\lim_{T\to0}\frac{N_2}{N_1}=\boxed{0}$$

That is, only the lower state would be populated.

E15.3(b) For two non-degenerate levels,

$$\frac{N_2}{N_1}=\mathrm{e}^{-\Delta\varepsilon/kT}\ \text{[Exercise 15.2(b)]}$$

$$\text{so}\quad \ln\frac{N_2}{N_1}=-\frac{\Delta\varepsilon}{kT}\quad\text{and}\quad T=-\frac{\Delta\varepsilon}{k\ln\dfrac{N_2}{N_1}}$$

$$\text{Thus,}\quad T=-\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times2.998\times10^{10}\,\mathrm{cm\,s^{-1}}\times300\,\mathrm{cm^{-1}}}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\times\ln(1/2)}=\boxed{623\,\mathrm{K}}$$

E15.4(b) In fact there are two upper states, but one upper level, and of course the answer is different if the question asks when 15% of the molecules are in the upper level, or if it asks when 15% of the molecules are in *each* upper state. The solution below assumes the former.

If the levels were non-degenerate, then

$$\frac{N_2}{N_1}=\mathrm{e}^{-\Delta\varepsilon/kT}\ \text{[Exercise 15.2(b)]}$$

Because each state at a given level is equally likely, the population ratio of the *levels* is

$$\frac{N_2}{N_1}=\frac{g_2\mathrm{e}^{-\beta\varepsilon_2}}{g_1\mathrm{e}^{-\beta\varepsilon_1}}=\frac{g_2}{g_1}\mathrm{e}^{-\Delta\varepsilon/kT}$$

Assuming that other states (if any) are negligibly populated,

$$\ln\frac{N_2}{N_1}=\ln\frac{g_2}{g_1}-\frac{\Delta\varepsilon}{kT}\quad\text{and}\quad T=-\frac{\Delta\varepsilon}{k\ln\dfrac{N_2g_1}{g_2N_1}}$$

$$\text{Thus,}\quad T=-\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times2.998\times10^{10}\,\mathrm{cm\,s^{-1}}\times360\,\mathrm{cm^{-1}}}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\times\ln\left(\dfrac{15\times1}{(100-15)\times2}\right)}=\boxed{21\bar{3}\,\mathrm{K}}$$

E15.5(b) (a) The thermal wavelength is

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} \; [15.19]$$

We need the molecular mass, not the molar mass:

$$m = \frac{20.18\times10^{-3}\,\text{kg mol}^{-1}}{6.022\times10^{23}\,\text{mol}^{-1}} = 3.351\times10^{-26}\,\text{kg}$$

So, $$\Lambda = \frac{6.626\times10^{-34}\,\text{J s}}{(2\pi\times3.351\times10^{-26}\,\text{kg}\times1.381\times10^{-23}\,\text{J K}^{-1}\times T)^{1/2}} = \frac{3.886\times10^{-10}\,\text{m}}{(T/\text{K})^{1/2}}$$

(i) $$T = 300\,\text{K}: \Lambda = \frac{3.886\times10^{-10}\,\text{m}}{(300)^{1/2}} = \boxed{2.243\times10^{-11}\,\text{m}} = \boxed{22.43\,\text{pm}}$$

(ii) $$T = 3000\,\text{K}: \Lambda = \frac{3.886\times10^{-10}\,\text{m}}{(3000)^{1/2}} = \boxed{7.094\times10^{-12}\,\text{m}} = \boxed{7.094\,\text{pm}}$$

(b) The translational partition function is

$$q^{\text{T}} = \frac{V}{\Lambda^3} \; [15.19]$$

(i) $$T = 300\,\text{K}: q^{\text{T}} = \frac{(1.00\times10^{-2}\,\text{m})^3}{(2.243\times10^{-11}\,\text{m})^3} = \boxed{8.86\times10^{25}}$$

(ii) $$T = 3000\,\text{K}: q^{\text{T}} = \frac{(1.00\times10^{-2}\,\text{m})^3}{(7.094\times10^{-12}\,\text{m})^3} = \boxed{2.80\times10^{27}}$$

E15.6(b) $$q^{\text{T}} = \frac{V}{\Lambda^3} \; [15.19] \text{ implying that } \frac{q}{q'} = \left(\frac{\Lambda'}{\Lambda}\right)^3$$

However, as $\Lambda \propto \dfrac{1}{m^{1/2}}$, $\dfrac{q}{q'} = \left(\dfrac{m}{m'}\right)^{3/2}$

so $$\frac{q_{\text{Xe}}}{q_{\text{He}}} = \left(\frac{m_{\text{Xe}}}{m_{\text{He}}}\right)^{3/2} = \left(\frac{131.3\,m_{\text{u}}}{4.003\,m_{\text{u}}}\right)^{3/2} = \boxed{187.9}$$

E15.7(b) $S = k \ln \mathcal{W}$ [15.27]

so $$\mathcal{W} = \mathrm{e}^{S/k} \quad \text{and} \quad \left(\frac{\partial \mathcal{W}}{\partial V}\right)_{T,N} = \frac{\mathrm{e}^{S/k}}{k}\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\mathcal{W}}{k}\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

$$S = nR \ln \frac{\mathrm{e}^{5/2}V}{N\Lambda^3} \; [15.39\text{a}] = nR\left(\ln V + \ln \frac{\mathrm{e}^{5/2}}{N\Lambda^3}\right),$$

so $$\left(\frac{\partial S}{\partial V}\right)_{T,N} = nR\left(\frac{\partial \ln V}{\partial V}\right)_{T,N} = \frac{nR}{V} = \frac{NR}{N_{\text{A}}V}$$

and $$\left(\frac{\partial \mathcal{W}}{\partial V}\right)_{T,N} = \frac{NR\mathcal{W}}{N_{\text{A}}kV} = \frac{N\mathcal{W}}{V}$$

$$\frac{\Delta\mathcal{W}}{\mathcal{W}} \approx N\frac{\Delta V}{V} = \frac{pV}{kT}\frac{\Delta V}{V} = \frac{(1\times10^{5}\,\text{Pa})\times(20\,\text{m}^{3})\times(1\times10^{-5})}{(1.381\times10^{-23}\,\text{J K}^{-1})\times(300\,\text{K})} = \boxed{4.8\times10^{21}}$$

Notice that the value of $\mathcal{W}$ is much larger than that of $\Delta\mathcal{W}/\mathcal{W}$. For example, at the conventional temperature the molar entropy of helium is 126 J K^{-1} mol^{-1}, therefore,

$$S = nS_{\text{m}} = \left(\frac{pV}{RT}\right)S_{\text{m}} = \frac{(1\times10^{5}\,\text{Pa})\times(20\,\text{m}^{3})\times(126\,\text{J K}^{-1}\,\text{mol}^{-1})}{(8.3145\,\text{J K}^{-1}\text{mol}^{-1})\times(298\,\text{K})} = 1.02\times10^{5}\,\text{J K}^{-1}$$

so $\dfrac{S}{k} = \dfrac{1.02\times10^{5}\,\text{J K}^{-1}}{1.381\times10^{-23}\,\text{J K}^{-1}} = 7.36\times10^{27}$

and $\mathcal{W} = \text{e}^{S/k} = \text{e}^{7.36\times10^{27}} = 10^{3.20\times10^{27}}$

E15.8(b) The high-temperature expression for the rotational partition function of a linear molecule is

$$q^{\text{R}} = \frac{kT}{\sigma hc\tilde{B}}\,[16.15\text{b}],\quad \tilde{B} = \frac{\hbar}{4\pi cI}\,[12.7],\ I = \mu R^{2}\,[\text{Table 12.1}]$$

Hence, $q = \dfrac{8\pi^{2}kTI}{\sigma h^{2}} = \dfrac{8\pi^{2}kT\mu R^{2}}{\sigma h^{2}}$

For N$_2$, $\mu = \frac{1}{2}m(\text{N}) = \frac{1}{2}\times14.007m_{\text{u}} = 7.00m_{\text{u}}$, and $\sigma = 2$, therefore

$$q = \frac{(8\pi^{2})\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(300\,\text{K})\times(7.00\times1.6605\times10^{-27}\,\text{kg})\times(1.0975\times10^{-10}\,\text{m})^{2}}{(2)\times(6.626\times10^{-34}\,\text{J s})^{2}}$$
$$= \boxed{52.2}$$

E15.9(b) The high-temperature expression for the rotational partition function of a non-linear molecule is

$$q^{\text{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}\,[16.14\text{b with }\sigma]$$

Combining the universal constants yields

$$\left(\frac{k}{hc}\right)^{3/2}\pi^{1/2} = \left(\frac{1.381\times10^{-23}\,\text{J K}^{-1}}{6.626\times10^{-34}\,\text{J s}\times2.998\times10^{10}\,\text{cm s}^{-1}}\right)^{3/2}\pi^{1/2} = 1.027\,\text{K}^{-3/2}\,\text{cm}^{-3/2}$$

Thus, $q^{\text{R}} = \dfrac{1.027}{\sigma}\dfrac{(T/\text{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\text{cm}^{-3})^{1/2}} = \dfrac{1.027\times(T/\text{K})^{3/2}}{(27.877\times14.512\times9.285)^{1/2}} = 0.01676\times(T/\text{K})^{3/2}$

(a) At 25°C, $q^{\text{R}} = 0.01676\times(298)^{3/2} = \boxed{86.2}$

(b) At 25°C, $q^{\text{R}} = 0.01676\times(373)^{3/2} = \boxed{121}$

E15.10(b) The rotational partition function of a non-symmetrical linear molecule is

$$q^{\text{R}} = \sum_{J}(2J+1)\text{e}^{-hc\tilde{B}J(J+1)/kT}\,[16.13\text{ with }\beta = 1/kT]$$

Use $\dfrac{hc\tilde{B}}{k} = \dfrac{6.626\times10^{-34}\,\text{J s}\times2.998\times10^{10}\,\text{cm s}^{-1}\times6.511\,\text{cm}^{-1}}{1.381\times10^{-23}\,\text{J K}^{-1}} = 9.366\,\text{K}$

so $q^{R} = \sum_{J} (2J+1)e^{-9.366\,\mathrm{K} \times J(J+1)/T}$

Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms until they converge. The high-temperature expression is

$$q^{R} = \frac{kT}{hc\tilde{B}} = \frac{T}{9.366\ \mathrm{K}}$$

The explicit and high-temperature expressions are compared in Figure 15.1. The difference between the two expressions is very nearly constant after the first few degrees. That difference drops to 5% of the explicit sum at $\boxed{62\ \mathrm{K}}$. As both expressions rise, their absolute difference becomes relatively smaller.

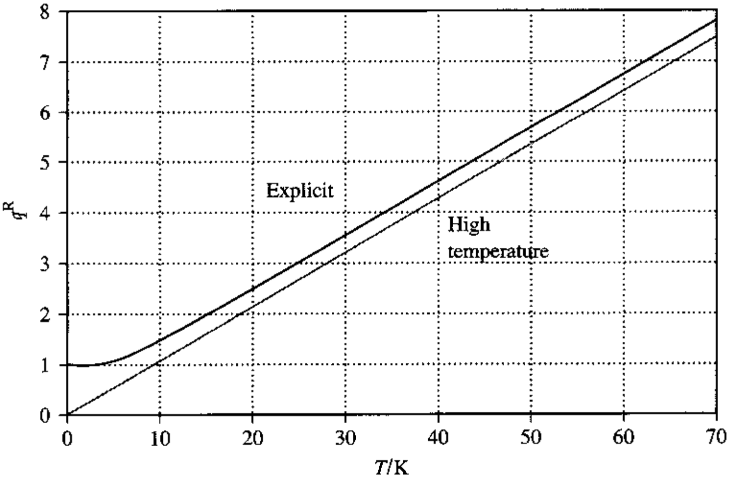


Figure 15.1

E15.11(b) The rotational partition function of a spherical rotor molecule, ignoring nuclear statistics, is

$$q^{R} = \sum_{J} g_J e^{-\varepsilon^{R}_{J}/kT}\ [15.9] = \sum_{J} (2J+1)^2 e^{-hc\tilde{B}J(J+1)/kT}\ [12.8 \text{ and Section } 12.4(\text{d})].$$

Use $\dfrac{hc\tilde{B}}{k} = \dfrac{6.626 \times 10^{-34}\ \mathrm{J\ s} \times 2.998 \times 10^{10}\ \mathrm{cm\ s^{-1}} \times 0.0572\ \mathrm{cm^{-1}}}{1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}} = 0.0823\ \mathrm{K}$

so $q^{R} = \sum_{J} (2J+1)^2 e^{-0.0823\,\mathrm{K} \times J(J+1)/T}$

Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms until they converge. The high-temperature expression is eqn 16.14b, neglecting σ and with $\tilde{A} = \tilde{B} = \tilde{C}$:

$$q^{R} = \pi^{1/2}\left(\frac{kT}{hc\tilde{B}}\right)^{3/2} = \pi^{1/2}\left(\frac{T}{0.0823\ \mathrm{K}}\right)^{3/2}$$

The explicit and high-temperature expressions are compared in Figure 15.2. The difference between the two expressions actually grows (albeit rather slowly) after the first few tenths of a degree. Because both expressions grow faster than does the difference between them, the relative difference drops; it reaches 5% of the explicit sum at $\boxed{0.4\ \mathrm{K}}$.

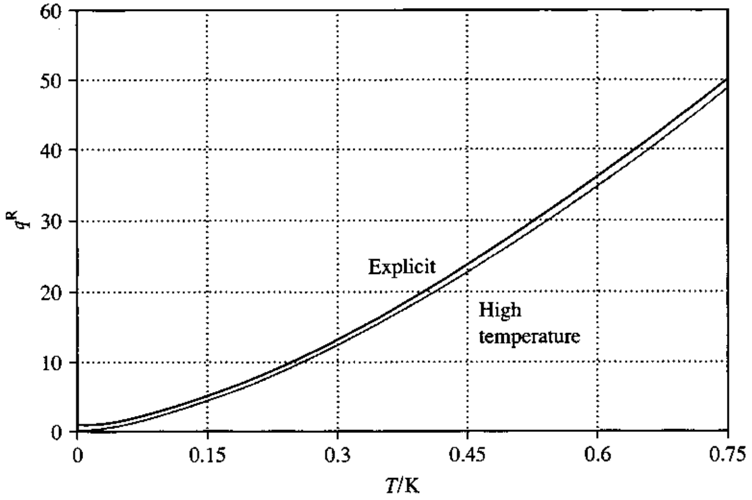


Figure 15.2

E15.12(b) The rotational partition function of a symmetric rotor molecule, ignoring nuclear statistics, is

$$q^{\mathrm{R}} = \sum_{J,K} g_{J,K}\mathrm{e}^{-\varepsilon^{\mathrm{R}}_{J,K}/kT}\,[15.9] = \sum_{J=0}(2J+1)\mathrm{e}^{-hc\tilde{B}J(J+1)/kT}\left(1+2\sum_{K=1}^{J}\mathrm{e}^{-hc(\tilde{A}-\tilde{B})K^2/kT}\right)[12.12]$$

Use $\dfrac{hc\tilde{B}}{k} = \dfrac{6.626\times10^{-34}\ \mathrm{J\ s}\times 2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times 9.444\ \mathrm{cm^{-1}}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}} = 13.585\ \mathrm{K}$, and

$$\frac{hc(\tilde{A}-\tilde{B})}{k} = \frac{6.626\times10^{-34}\ \mathrm{J\ s}\times 2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times(6.196-9.444)\ \mathrm{cm^{-1}}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}}$$

$$= -4.672\ \mathrm{K}$$

so $\quad q^{\mathrm{R}} = \sum_{J=0}(2J+1)\mathrm{e}^{-13.585\,\mathrm{K}\times J(J+1)/T}\left(1+2\sum_{K=1}^{J}\mathrm{e}^{+4.672\,\mathrm{K}\times K^2/T}\right)$

Write a brief computer program or use other mathematical software to evaluate the terms of the sum and to sum the terms until they converge. Nested sums are straightforward to program in languages such as BASIC or FORTRAN, whereas in spreadsheets they are more unwieldy. Compare the results of the direct sum with the high-temperature expression, eqn 16.14b, with $\tilde{B} = \tilde{C}$:

$$q^{\mathrm{R}} = \left(\frac{\pi}{\tilde{A}}\right)^{1/2}\left(\frac{kT}{hc}\right)^{3/2}\frac{1}{\tilde{B}}$$

The explicit and high-temperature expressions are compared in Figure 15.3. The difference between the two expressions actually grows (albeit rather slowly) after the first few degrees. Because both expressions grow faster than does the difference between them, the relative difference drops; it reaches 5% of the explicit sum at $\boxed{55\ \mathrm{K}}$.

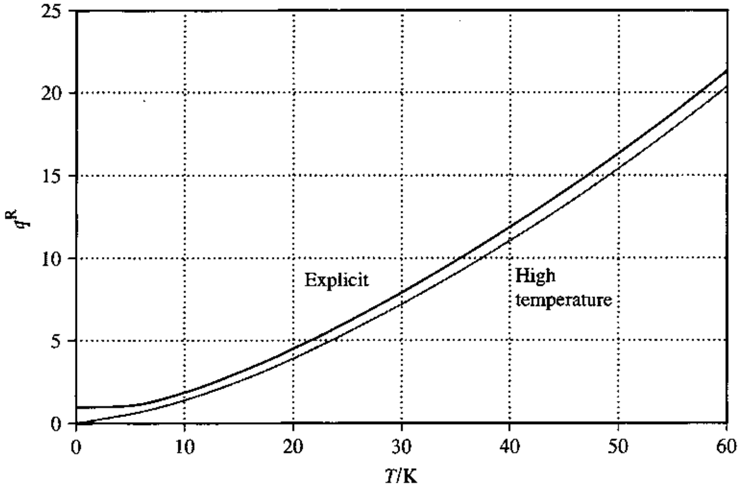


Figure 15.3

E15.13(b) The symmetry number is the order of the rotational subgroup of the group to which a molecule belongs (except for linear molecules, for which $\sigma = 2$ if the molecule has inversion symmetry and 1 otherwise). The rotational subgroup contains only rotational operations and the identity.

(a) CO_2: full group $D_{\infty h}$; subgroup C_2; hence $\sigma = \boxed{2}$

(b) O_3: full group C_{2v}; subgroup C_2; $\sigma = \boxed{2}$

(c) SO_3: full group D_{3h}; subgroup $\{E, C_3, C_3^2, 3C_2\}$; $\sigma = \boxed{6}$

(d) SF_6: full group O_h; subgroup O; $\sigma = \boxed{24}$

(e) Al_2Cl_6: full group D_{2d}; subgroup D_2; $\sigma = \boxed{4}$

E15.14(b) Pyridine belongs to the C_{2v} group, the same as water, so $\sigma = 2$. The rotational partition function of a non-linear molecule is [Exercise 15.9(a)]

$$q^R = \frac{1.027}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3})^{1/2}} = \frac{1.027 \times (298.15)^{3/2}}{2 \times (0.2014 \times 0.1936 \times 0.0987)^{1/2}} = \boxed{4.26 \times 10^4}$$

E15.15(b) The partition function for a mode of molecular vibration is

$$q^V = \sum_v e^{-vhc\tilde{\nu}/kT} = \frac{1}{1 - e^{-hc\tilde{\nu}/kT}} \ [16.19 \text{ with } \beta = 1/kT]$$

Use $\dfrac{hc\tilde{\nu}}{k} = \dfrac{6.626 \times 10^{-34}\ \mathrm{J\ s} \times 2.998 \times 10^{10}\ \mathrm{cm\ s^{-1}} \times 214.5\ \mathrm{cm^{-1}}}{1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}} = 308.5\ \mathrm{K}$

so $q^V = \displaystyle\sum_v e^{-vhc\tilde{\nu}/kT} = \frac{1}{1 - e^{-308.5\,\mathrm{K}/T}}$

The high-temperature expression is

$$q^V = \frac{kT}{hc\tilde{\nu}} = \frac{T}{308.5\ \mathrm{K}} \ [16.21]$$

The explicit and high-temperature expressions are compared in Figure 15.4. The high-temperature expression reaches 95% of the explicit sum at $\boxed{3000\text{ K}}$.

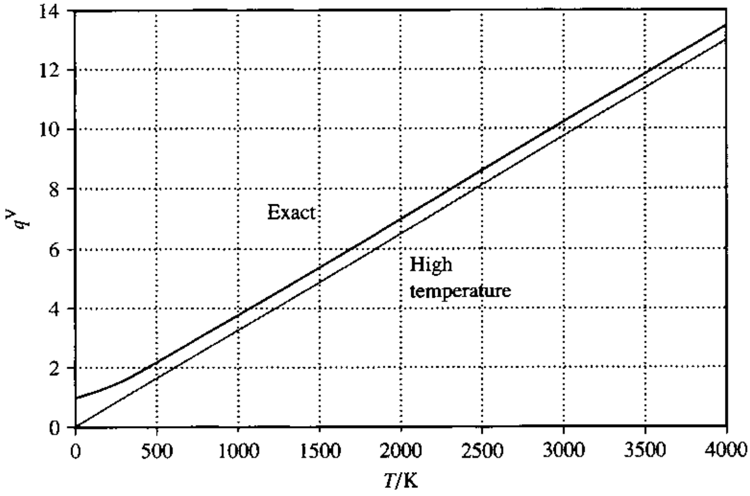


Figure 15.4

E15.16(b) The partition function for a mode of molecular vibration is

$$q^{V}_{\text{mode}} = \sum_{v} e^{-vhc\tilde{\nu}/kT} = \frac{1}{1-e^{-hc\tilde{\nu}/kT}} \;[16.19 \text{ with } \beta = 1/kT]$$

and the overall vibrational partition function is the product of the partition functions of the individual modes. (See Example 16.3.) We draw up the following table:

Mode	1	2	3	4
$\tilde{\nu}/\text{cm}^{-1}$	3311	712	712	2097
$hc\tilde{\nu}/kT$	5.292	1.138	1.138	3.352
q^{V}_{mode}	1.005	1.472	1.472	1.036

The overall vibrational partition function is

$$q^{V} = 1.005 \times 1.472 \times 1.472 \times 1.036 = \boxed{2.256}$$

E15.17(b) The partition function for a mode of molecular vibration is

$$q^{V}_{\text{mode}} = \sum_{v} e^{-vhc\tilde{\nu}/kT} = \frac{1}{1-e^{-hc\tilde{\nu}/kT}} \;[16.19 \text{ with } \beta = 1/kT]$$

and the overall vibrational partition function is the product of the partition functions of the individual modes. (See Example 16.3.) We draw up the following table, including the degeneracy of each level:

Mode	1	2	3	4
$\tilde{\nu}/\text{cm}^{-1}$	178	90	555	125
g_{mode}	1	2	3	3
$hc\tilde{\nu}/kT$	0.512	0.259	1.597	0.360
$q^{\text{V}}_{\text{mode}}$	2.50	4.38	1.254	3.31

The overall vibrational partition function is

$$q^{\text{V}} = 2.50 \times 4.38^2 \times 1.254^3 \times 3.31^3 = \boxed{3.43 \times 10^3}$$

E15.18(b)

$$q = \sum_{\text{levels}} g_j \text{e}^{-\beta\varepsilon_j}\,[15.9] = \sum_{\text{levels}} g_j \text{e}^{-hc\tilde{\nu}_j/kT} = 2 + 3\text{e}^{-hc\tilde{\nu}_1/kT} + 2\text{e}^{-hc\tilde{\nu}_2/kT}$$

where $\dfrac{hc\tilde{\nu}_j}{kT} = \dfrac{6.626 \times 10^{-34}\,\text{J s} \times 2.998 \times 10^{10}\,\text{cm s}^{-1} \times \tilde{\nu}_j}{1.381 \times 10^{-23}\,\text{J K}^{-1} \times 2000\,\text{K}} = 7.192 \times 10^{-4} \times (\tilde{\nu}_j/\text{cm}^{-1})$

Therefore,

$$q = 2 + 3\text{e}^{-7.192\times10^{-4}\times1250} + 2\text{e}^{-7.192\times10^{-4}\times1300} = 2 + 3 \times 0.4070 + 2 \times 0.3926 = \boxed{4.0061}$$

E15.19(b)

$$U_{\text{m}} - U_{\text{m}}(0) = -\frac{N_{\text{A}}}{q}\left(\frac{\text{d}q}{\text{d}\beta}\right)_V \;[15.24\text{a for 1 mol}]$$

Use $\dfrac{hc\tilde{\nu}_j}{kT} = hc\tilde{\nu}_j\beta = 7.192 \times 10^{-4}\tilde{\nu}_j$ [Exercise 15.18(b)]

and $q = 2 + 3\text{e}^{-hc\tilde{\nu}_1\beta} + 2\text{e}^{-hc\tilde{\nu}_2\beta} = 4.0061$ [Exercise 15.18(b)]

Thus, $U_{\text{m}} - U_{\text{m}}(0) = -\dfrac{N_{\text{A}}hc}{q}(3\tilde{\nu}_1\text{e}^{-hc\tilde{\nu}_1\beta} + 2\tilde{\nu}_2\text{e}^{-hc\tilde{\nu}_2\beta})$

$$= \frac{6.022 \times 10^{23}\,\text{mol}^{-1} \times 6.626 \times 10^{-34}\,\text{J s} \times 2.998 \times 10^{10}\,\text{cm s}^{-1}}{4.0061}$$

$$\times (3 \times 1250\,\text{cm}^{-1} \times \text{e}^{-7.192\times10^{-4}\times1250} + 2 \times 1300\,\text{cm}^{-1} \times \text{e}^{-7.192\times10^{-4}\times1300})$$

$$= \boxed{+7.61 \times 10^3\,\text{J}} = \boxed{+7.61\,\text{kJ}}$$

E15.20(b) The energies of the states relative to the energy of the state with $m_l = 0$ are $-\gamma\hbar\mathcal{B}$, 0, and $+\gamma\hbar\mathcal{B}$. With respect to the lowest level they are 0, $\gamma\hbar\mathcal{B}$ and $2\gamma\hbar\mathcal{B}$, respectively. The partition function is

$$q = \sum_i \text{e}^{-\beta\varepsilon_i} = \boxed{1 + \text{e}^{-\gamma\hbar\mathcal{B}\beta} + \text{e}^{-2\gamma\hbar\mathcal{B}\beta}}$$

where the energies are measured with respect to the lowest energy.

The mean energy per electron is

$$\langle\varepsilon\rangle = \frac{E(T)}{N} = -\frac{1}{q}\frac{\text{d}q}{\text{d}\beta} = \frac{\gamma\hbar\mathcal{B}(\text{e}^{-\gamma\hbar\mathcal{B}\beta} + 2\text{e}^{-2\gamma\hbar\mathcal{B}\beta})}{1 + \text{e}^{-\gamma\hbar\mathcal{B}\beta} + \text{e}^{-2\gamma\hbar\mathcal{B}\beta}} = \boxed{\frac{\gamma\hbar\mathcal{B}(1 + 2\text{e}^{-\gamma\hbar\mathcal{B}\beta})}{\text{e}^{\gamma\hbar\mathcal{B}\beta} + 1 + \text{e}^{-\gamma\hbar\mathcal{B}\beta}}}\;[15.22]$$

Alternatively, if we measure energy with respect to zero magnetic field (rather than to ground-state energy), then

$$\langle\varepsilon\rangle = \varepsilon_{\mathrm{gs}} - \frac{1}{q}\frac{\mathrm{d}q}{\mathrm{d}\beta} = -\gamma\hbar\mathcal{B} + \frac{\gamma\hbar\mathcal{B}(1+2\mathrm{e}^{-\gamma_{\mathrm{N}}\hbar\mathcal{B}\beta})}{\mathrm{e}^{\gamma_{\mathrm{N}}\hbar\mathcal{B}\beta}+1+\mathrm{e}^{-\gamma_{\mathrm{N}}\hbar\mathcal{B}\beta}} = \boxed{\gamma\hbar\mathcal{B}\left(\frac{1+2\mathrm{e}^{-\gamma_{\mathrm{N}}\hbar\mathcal{B}\beta}}{\mathrm{e}^{\gamma_{\mathrm{N}}\hbar\mathcal{B}\beta}+1+\mathrm{e}^{-\gamma_{\mathrm{N}}\hbar\mathcal{B}\beta}}-1\right)}$$

Letting $x = \gamma\hbar\beta\mathcal{B}$, the partition function becomes

$$q = 1 + \mathrm{e}^{-x} + \mathrm{e}^{-2x}$$

and the mean energy, scaled by the energy separation, becomes

$$\frac{\langle\varepsilon\rangle}{\gamma\hbar\mathcal{B}} = \frac{1+2\mathrm{e}^{-x}}{\mathrm{e}^{x}+1+\mathrm{e}^{-x}} - 1$$

The functions are plotted in Figures 15.5(a) and (b). The effect of increasing the magnetic field is to concentrate population into the lower level.

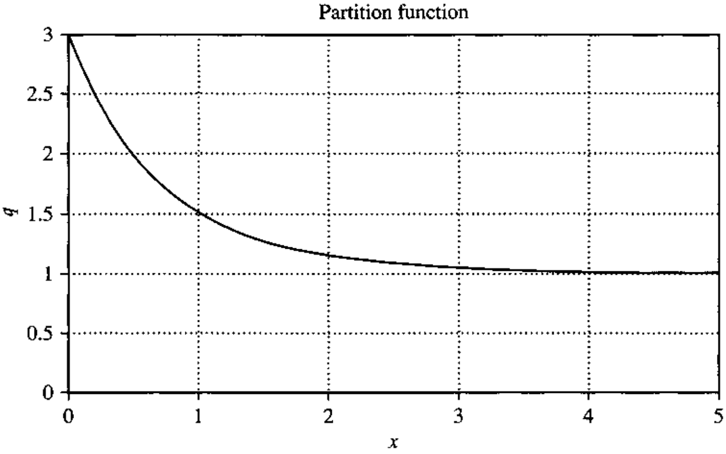


Figure 15.5(a)

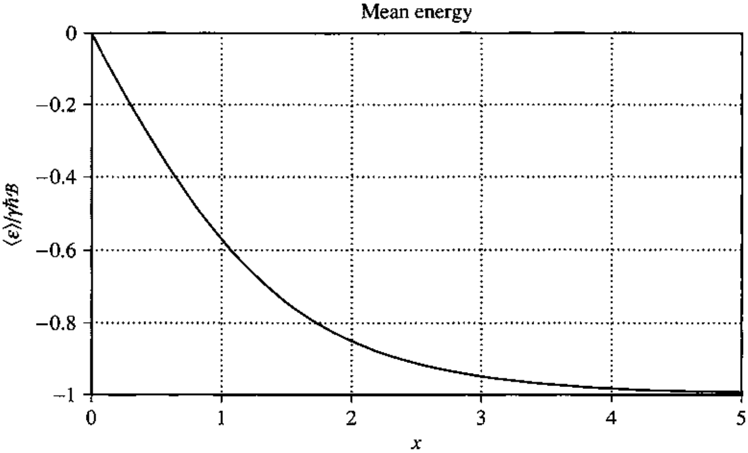


Figure 15.5(b)

Expressions for the relative populations are given in Exercise 15.2(b).

The relative populations are

$$\frac{N_+}{N_-} = e^{-\beta\Delta\varepsilon} = e^{-2\gamma\hbar\mathcal{B}\beta} = e^{-2x} \quad \text{and} \quad \frac{N_0}{N_-} = e^{-\gamma\hbar\mathcal{B}\beta} = e^{-x}$$

$$\text{where } x = \gamma\hbar\mathcal{B}\beta = \frac{\gamma\hbar\mathcal{B}}{kT} = \frac{1.933\times10^{7}\,\mathrm{T^{-1}\,s^{-1}}\times1.0546\times10^{-34}\,\mathrm{J\,s}\times20.0\,\mathrm{T}}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})T}$$

$$= \frac{2.95\times10^{-3}}{T/\mathrm{K}}$$

Because x is so small, the population ratios will be close to 1, even at low temperature. Thus, it will be more informative to report the difference of the ratios from 1, using the series expansion of the exponentials:

$$1-\frac{N_+}{N_-} = 1-e^{-2x} \approx 2x \quad \text{and} \quad 1-\frac{N_0}{N_-} = 1-e^{-x} \approx x$$

(a) $1-\frac{N_+}{N_-} \approx 2x = \frac{2\times2.95\times10^{-3}}{1.0} = 5.9\times10^{-3}$ and $1-\frac{N_0}{N_-} = 2.95\times10^{-3}$

(b) $1-\frac{N_+}{N_-} = \frac{2\times2.95\times10^{-3}}{298} = 2.0\times10^{-5}$ and $1-\frac{N_0}{N_-} = \frac{2.95\times10^{-3}}{298} = 1.0\times10^{-5}$

E15.21(b) (a) The ratio of populations is given by the Boltzmann factor

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = e^{-25.0\,\mathrm{K}/T} \quad \text{and} \quad \frac{n_3}{n_1} = e^{-50.0\,\mathrm{K}/T}$$

(1) At 1.00 K, $\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{1.00\,\mathrm{K}}\right) = \boxed{1.39\times10^{-11}}$ and $\frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{1.00\,\mathrm{K}}\right) = \boxed{1.93\times10^{-22}}$

(2) At 25.0 K, $\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{25.0\,\mathrm{K}}\right) = \boxed{0.368}$ and $\frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{25.0\,\mathrm{K}}\right) = \boxed{0.135}$

(3) At 100 K, $\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{100\,\mathrm{K}}\right) = \boxed{0.779}$ and $\frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{100\,\mathrm{K}}\right) = \boxed{0.607}$

(b) The molecular partition function is

$$q = \sum_{\text{states}} e^{-\varepsilon_{\text{state}}/kT} = 1 + e^{-25.0\,K/T} + e^{-50.0\,K/T}$$

At 25.0 K, we note that $e^{-25.0\,K/T} = e^{-1}$ and $e^{-50.0\,K/T} = e^{-2}$

$$q = 1 + e^{-1} + e^{-2} = 1.503$$

(c) $E(T) = -\frac{N}{q}\frac{dq}{d\beta}$ [15.22]

So $E_m(T) = -\frac{N_A}{q}(-25.0\,\mathrm{K})k(e^{-25.0\,\mathrm{K}/T} + 2e^{-50.0\,\mathrm{K}/T})$

At 25.0 K, $E_{\rm m} = -\dfrac{(6.022\times10^{23}\,\text{mol}^{-1})\times(-25.0\,\text{K})\times(1.381\times10^{-23}\,\text{J K}^{-1})}{1.503}\times(\text{e}^{-1}+2\text{e}^{-2})$

$$= \boxed{88.3\ \text{J mol}^{-1}}$$

(d) The molar heat capacity is

$$C_{V,\rm m} = \left(\frac{\partial U_{\rm m}}{\partial T}\right)_V = N_{\rm A}(25.0\,\text{K})k\frac{\partial}{\partial T}\frac{1}{q}(\text{e}^{-25.0K/T}+2\text{e}^{-50.0K/T})$$

$$= N_{\rm A}(25.0\text{K})k\times\left(\frac{25.0\,\text{K}}{qT^2}(\text{e}^{-25.0K/T}+4\text{e}^{-50.0K/T})-\frac{1}{q^2}(\text{e}^{-25.0K/T}+2\text{e}^{-50.0K/T})\frac{\partial q}{\partial T}\right)$$

where $\dfrac{\partial q}{\partial T} = \dfrac{25.0\,\text{K}}{T^2}(\text{e}^{-25.0\text{K}/T}+2\text{e}^{-50.0\text{K}/T})$

so $\quad C_{V,\rm m} = \dfrac{N_{\rm A}(25.0\,\text{K})^2k}{T^2q}\left(\text{e}^{-25.0K/T}+4\text{e}^{-50.0K/T}-\dfrac{(\text{e}^{-25.0\text{K}/T}+2\text{e}^{-50.0\text{K}/T})^2}{q}\right)$

At 25.0 K, $C_{V,\rm m} = \dfrac{(6.022\times10^{23}\,\text{mol}^{-1})\times(25.0\,\text{K})^2\times(1.381\times10^{-23}\,\text{J K}^{-1})}{(25.0\,\text{K})^2\times(1.503)}$

$$\times\left(\text{e}^{-1}+4\text{e}^{-2}-\frac{(\text{e}^{-1}+2\text{e}^{-2})^2}{1.503}\right)$$

$$= \boxed{3.53\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

(e) The molar entropy is

$$S_{\rm m} = \frac{U_{\rm m}-U_{\rm m}(0)}{T}+N_{\rm A}k\ln q$$

At 25.0 K, $S_{\rm m} = \dfrac{88.3\,\text{J mol}^{-1}}{25.0\,\text{K}}+(6.022\times10^{23}\,\text{mol}^{-1})\times(1.381\times10^{-23}\,\text{J K}^{-1})\ln 1.503$

$$= \boxed{6.92\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

E15.22(b) $\quad \dfrac{n_1}{n_0} = \dfrac{g_1\text{e}^{-\varepsilon_1/kT}}{g_0\text{e}^{-\varepsilon_0/kT}} = g_1\text{e}^{-\Delta\varepsilon/kT} = 3\text{e}^{-2hc\tilde{B}/kT}\,[12.10]$

Set $\dfrac{n_1}{n_0} = \dfrac{1}{\text{e}}$ and solve for T.

$$\ln\left(\frac{1}{\text{e}}\right) = -1 = \ln 3+\left(\frac{-2hc\tilde{B}}{kT}\right)$$

$$T = \frac{2hc\tilde{B}}{k(1+\ln 3)}$$

$$= \frac{2\times(6.626\times10^{-34}\,\text{J s})\times2.998\times10^{10}\,\text{cm s}^{-1}\times10.59\,\text{cm}^{-1}}{1.381\times10^{-23}\,\text{J K}^{-1}\times(1+1.0986)} = \boxed{14.52\ \text{K}}$$

where we used $\tilde{B} = 10.59\,\text{cm}^{-1}$ from Table 12.2, assuming $^1\text{H}^{35}\text{Cl}$.

E15.23(b) The Sackur–Tetrode equation gives the statistical entropy; for 1 mole at standard pressure:

$$S_m^{\ominus} = R\ln\left(\frac{e^{5/2}kT}{p^{\ominus}\Lambda^3}\right)[15.39b], \text{ where } \Lambda = \frac{h}{(2\pi mkT)^{1/2}}[15.19]$$

(a) At 100 K

$$\Lambda = \frac{6.626\times10^{-34}\ \mathrm{J\ s}}{\{2\pi(131.3)(1.6605\times10^{-27}\ \mathrm{kg})(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(100\ \mathrm{K})\}^{1/2}} = 1.52\times10^{-11}\ \mathrm{m}$$

$$S_m^{\ominus} = (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\left(\frac{e^{5/2}(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(100\ \mathrm{K})}{(10^5\ \mathrm{Pa})\times(1.52\times10^{-11}\ \mathrm{m})^3}\right) = \boxed{147\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

(b) At 298.15 K

$$\Lambda = \frac{6.626\times10^{-34}\ \mathrm{J\ s}}{\{2\pi(131.3)(1.6605\times10^{-27}\ \mathrm{kg})(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298.15\ \mathrm{K})\}^{1/2}}$$
$$= 8.823\times10^{-12}\ \mathrm{m}$$

and $S_m^{\ominus} = (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\left(\dfrac{e^{5/2}(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298.15\ \mathrm{K})}{(10^5\ \mathrm{Pa})\times(8.823\times10^{-12}\ \mathrm{m})^3}\right)$

$$= \boxed{169.6\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

E15.24(b) The entropy in terms of partition function is

$$S(T) = \frac{U(T)-U(0)}{T} + Nk\ln q\,[15.28] = -\frac{N}{T}\left(\frac{\partial \ln q}{\partial \beta}\right)_V + Nk\ln q\,[15.24b]$$

$$q = \frac{1}{1-e^{-\beta\varepsilon}}\,[\text{Example } 15.2] = \frac{1}{1-e^{-hc\beta\tilde{\nu}}}$$

and $\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V = (1-e^{-hc\beta\tilde{\nu}})\times\dfrac{-hc\tilde{\nu}e^{-hc\beta\tilde{\nu}}}{(1-e^{-hc\beta\tilde{\nu}})^2} = -\dfrac{hc\tilde{\nu}e^{-hc\beta\tilde{\nu}}}{1-e^{-hc\beta\tilde{\nu}}} = -\dfrac{hc\tilde{\nu}}{e^{hc\beta\tilde{\nu}}-1}$

$$hc\beta\tilde{\nu} = \frac{(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times(321\ \mathrm{cm^{-1}})}{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(600\ \mathrm{K})} = 0.7696$$

Therefore, $q = \dfrac{1}{1-e^{-0.7696}} = 1.863$

and $\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V = -\dfrac{(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times(321\ \mathrm{cm^{-1}})}{e^{0.7696}-1}$

$$= -5.503\times10^{-21}\ \mathrm{J}$$

Hence, $S_m = (6.022\times10^{23}\ \mathrm{mol^{-1}})\times\left(\dfrac{5.503\times10^{-21}\ \mathrm{J}}{600\ \mathrm{K}} + (1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\ln 1.863\right)$

$$= \boxed{10.70\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

E15.25(b) Inclusion of a factor of $1/N!$ is necessary when considering indistinguishable particles. Because of their translational freedom, gases are collections of indistinguishable particles. The factor, then, must be included in calculations on (a) $\boxed{\mathrm{CO_2\ gas}}$.

Solutions to problems

Solutions to numerical problems

P15.2 Number of configurations of combined system, $\mathcal{W} = \mathcal{W}_1\mathcal{W}_2$

$$\mathcal{W} = (10^{20}) \times (2 \times 10^{20}) = \boxed{2 \times 10^{40}}.$$

$$S = k \ln \mathcal{W}\,[15.27] = (1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times \ln(2 \times 10^{40}) = \boxed{1.282 \times 10^{-21}\ \mathrm{J\,K^{-1}}}$$

$$S_1 = k \ln \mathcal{W}_1 = (1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times \ln(10^{20}) = \boxed{0.636 \times 10^{-21}\ \mathrm{J\,K^{-1}}}$$

$$S_2 = k \ln \mathcal{W}_2 = (1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times \ln(2 \times 10^{20}) = \boxed{0.646 \times 10^{-21}\ \mathrm{J\,K^{-1}}}$$

These results are significant in that they show that the statistical-mechanical entropy is an additive property consistent with the thermodynamic result. That is,

$$S = S_1 + S_2 = (0.636 + 0.646) \times 10^{-21}\ \mathrm{J\,K^{-1}} = 1.282 \times 10^{-21}\ \mathrm{J\,K^{-1}}$$

P15.4 This problem can be carried out on a spreadsheet if care is taken with the layout. One may simply pick values of $\tilde{\nu}$; however, if one works in terms of the characteristic vibrational temperature, θ_V, one can employ more general dimensionless quantities, as described below.

$$\theta_V = \frac{hc\tilde{\nu}}{k}\ \text{[Section 16.2(c)]}$$

We note that the energy levels of the Morse oscillator can be written as

$$\begin{aligned} E_v &= (v + \tfrac{1}{2})hc\tilde{\nu} - (v + \tfrac{1}{2})^2 x_e hc\tilde{\nu}\ [12.38] \\ &= (v + \tfrac{1}{2})k\theta_V - (v + \tfrac{1}{2})^2 x_e k\theta_V = (v + \tfrac{1}{2})k\theta_V\{1 - (v + \tfrac{1}{2})x_e\} \end{aligned}$$

Thus, one can tabulate values of $E_v/k\theta_V$ without having to select a wavenumber. Similarly, one can employ the dimensionless temperature T/θ_V. As noted in the problem, Boltzmann factors require energies measured with respect to the ground state, so the energies in the exponents of the Boltzmann factors must be $E_v - E_0$. The energy expression for the Morse oscillator eventually reaches a maximum in v and then begins decreasing. Only the states up to and including the maximum energy are physically meaningful, so there are a finite number of Morse states. Thus, the partition function for a Morse oscillator is:

$$q = \sum_{v=0}^{v_{\max}} \exp\left(-\frac{E_v - E_0}{kT}\right) = \sum_{v=0}^{v_{\max}} \exp\left(-\frac{E_v - E_0}{k\theta_V} \times \frac{\theta_V}{T}\right)$$

To choose meaningful values of the anharmonicity, x_e, look up vibrational constants for some common diatomic molecules. x_e is about 0.03 for H_2 and about an order of magnitude smaller for I_2.

A plot of partition functions with various anharmonicities is shown in Figure 15.6. For small values of x_e, the partition function closely resembles that of a harmonic oscillator [15.12]. This provides a check on the calculation, for a Morse oscillator in the limit of small x_e *is* a harmonic oscillator. As x_e increases, the partition function gradually increases compared to the harmonic oscillator. This reflects the fact that the Morse oscillator energy levels become more closely spaced with increasing energy, so more levels are accessible at a given temperature. Eventually, however, the

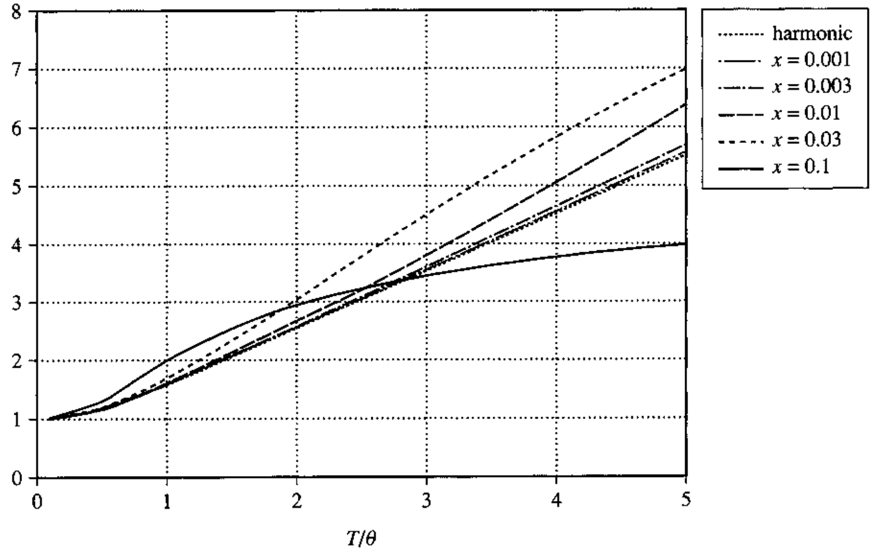


Figure 15.6

partition functions of highly anharmonic Morse oscillators fall below the harmonic curve at high temperatures. This reflects the fact that these Morse oscillators have a finite number of energy levels (indeed, a small number) so naturally a harmonic oscillator has more accessible levels at high temperature.

P15.6 If the electronic states were in thermal equilibrium with the translational states, then the temperature would be the same for both. The ratio of electronic states at 300 K would be

$$\frac{N_1}{N_0}=\frac{g_1 e^{-\varepsilon_1/kT}}{g_0 e^{-\varepsilon_0/kT}}=\frac{4}{2}\times e^{-\Delta\varepsilon/kT}=2e^{-hc\tilde{\nu}/kT}$$

$$=2\exp\left(-\frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})\times(450\,\mathrm{cm^{-1}})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(300\,\mathrm{K})}\right)=0.23$$

The observed ratio is $\frac{0.30}{0.70}=0.43$. Hence, the populations are $\boxed{\text{not at equilibrium}}$.

P15.8 (a) First, evaluate the partition function

$$q=\sum_J g_J e^{-\beta\varepsilon_J}\,[15.9]=\sum_J g_J e^{-hc\beta\tilde{\nu}_J}$$

The degeneracy is given by

$$g_J=2J+1$$

where J is the level of the term (displayed as the subscript in the term symbol).

At 3287°C = 3560 K, $hc\beta=\dfrac{6.626\times10^{-34}\,\mathrm{J\,s}\times2.998\times10^{10}\,\mathrm{cm\,s^{-1}}}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\times3560\,\mathrm{K}}=4.041\times10^{-4}\,\mathrm{cm}$

$$q=5+7e^{-\{(4.041\times10^{-4}\mathrm{cm})\times(170\,\mathrm{cm^{-1}})\}}+9e^{-\{(4.041\times10^{-4}\mathrm{cm})\times(387\mathrm{cm^{-1}})\}}+3e^{-\{(4.041\times10^{-4}\mathrm{cm})\times(6557\,\mathrm{cm^{-1}})\}}$$

$$=5+7\times(0.934)+9\times(0.855)+3\times(0.0707)=19.444$$

The fractions of molecules in the various energy levels are

$$p_I = \frac{g_I e^{-\beta\varepsilon_I}}{q} = \frac{g_I e^{-hc\beta\tilde{\nu}_I}}{q} \text{ [15.7, with degeneracy included]}$$

$$p(^3F_2) = \frac{5}{19.444} = \boxed{0.257} \qquad p(^3F_3) = \frac{(7)\times(0.934)}{19.444} = \boxed{0.336}$$

$$p(^3F_4) = \frac{(9)\times(0.855)}{19.444} = \boxed{0.396} \qquad p(^4F_1) = \frac{(3)\times(0.0707)}{19.444} = \boxed{0.011}$$

COMMENT. $\sum_I p_I = 1$. Note that the most highly populated level is not the lowest level.

P15.10 The partition function is

$$q = \sum_I g_I e^{-\beta\varepsilon_I} \text{ [15.9]} = \sum_I g_I e^{-hc\beta\tilde{\nu}_I} = \sum_I g_I e^{-hc\tilde{\nu}_I/kT}$$

The degeneracy is given by

$$g_I = 2J + 1$$

where J is the level of the term (displayed as the subscript in the term symbol).

$$\text{At 298 K, } \frac{hc\tilde{\nu}_I}{kT} = \frac{6.626\times10^{-34}\text{ J s}\times2.998\times10^{10}\text{ cm s}^{-1}\times\tilde{\nu}_I}{1.381\times10^{-23}\text{ J K}^{-1}\times(298\text{ K})} = 4.83\times10^{-3}\times\frac{\tilde{\nu}_I}{\text{cm}^{-1}}$$

$$\text{so}\quad q = 1 + 3e^{-4.83\times10^{-3}\times557.1} + 5e^{-4.83\times10^{-3}\times1410.0} + 5e^{-4.83\times10^{-3}\times7125.3} + e^{-4.83\times10^{-3}\times16367.3} = \boxed{1.209}$$

$$\text{At 1000 K, } \frac{hc\tilde{\nu}_I}{kT} = \frac{6.626\times10^{-34}\text{ J s}\times2.998\times10^{10}\text{ cm s}^{-1}\times\tilde{\nu}_I}{1.381\times10^{-23}\text{ J K}^{-1}\times(1000\text{ K})} = 1.439\times10^{-3}\times\frac{\tilde{\nu}_I}{\text{cm}^{-1}}$$

$$\text{so}\quad q = 1 + 3e^{-1.439\times10^{-3}\times557.1} + 5e^{-1.439\times10^{-3}\times1410.0} + 5e^{-1.439\times10^{-3}\times7125.3} + e^{-1.439\times10^{-3}\times16367.3} = \boxed{3.004}$$

P15.12 (a) Total entropy: $S = S_1 + S_2 = (5.69 + 11.63)\text{ J K}^{-1} = 17.32\text{ J K}^{-1}$

$$\mathcal{W} = e^{S/k}\text{ [from 15.27]} = e^{17.32\text{ J K}^{-1}/1.381\times10^{-23}\text{ J K}^{-1}} = e^{1.254\times10^{24}} = \boxed{10^{5.44\times10^{23}}}$$

(b) Total entropy, $S = 2\text{ mol}\times(9.03\text{ J K}^{-1}\text{ mol}^{-1}) = 18.06\text{ J K}^{-1}$

$$\mathcal{W} = e^{S/k} = e^{18.06\text{ J K}^{-1}/1.381\times10^{-23}\text{ J K}^{-1}} = e^{1.31\times10^{24}} = \boxed{10^{5.69\times10^{23}}}$$

The final temperature is not the average because the molar heat capacity of graphite increases with temperature. At 298 K, it is 8.54 J K^{-1} mol^{-1}, whereas at 498 K it is 14.64 J K^{-1} mol^{-1}.

(c) At constant internal energy and volume the condition for spontaneity is $\Delta S_{U,V} > 0$. Since $\mathcal{W}_{(b)} > \mathcal{W}_{(a)}$, the process of part (b) is $\boxed{\text{spontaneous}}$.

Solutions to theoretical problems

P15.14 (a) $\mathcal{W} = \dfrac{N!}{N_0!N_1!N_2!\cdots}\text{ [13.1]} = \dfrac{5!}{0!5!0!0!0!} = \boxed{1}$

(b) We draw up the following table:

0	ε	2ε	3ε	4ε	5ε	$\mathcal{W}=\dfrac{N!}{n_1!n_2!\ldots}$
4	0	0	0	0	1	5
3	1	0	0	1	0	20
3	0	1	1	0	0	20
2	2	0	1	0	0	30
2	1	2	0	0	0	30
1	3	1	0	0	0	20
0	5	0	0	0	0	1

The most probable configurations are $\boxed{\{2,2,0,1,0,0\}}$ and $\boxed{\{2,1,2,0,0,0\}}$.

P15.16 (a) The probability of finding a molecule in state j is

$$p_j=\frac{N_j}{N}=\frac{\mathrm{e}^{-\beta\varepsilon_j}}{q}\ [15.7]$$

In the systems under consideration, ε is both the mean energy and the energy difference between adjacent levels, so

$$p_j=\frac{\mathrm{e}^{-j\beta\varepsilon}}{q}$$

which implies that

$$-j\beta\varepsilon=\ln N_j-\ln N+\ln q \quad \text{and} \quad \ln N_j=\ln N-\ln q-j\beta\varepsilon=\boxed{\ln\frac{N}{q}-\frac{j\varepsilon}{kT}}$$

Thus, a plot of $\ln N_j$ against j should be a straight line with slope $-\varepsilon/kT$.

We draw up the following table using the information in Problem 15.15:

j	0	1	2	3	
N_j	4	2	2	1	[most probable configuration]
$\ln N_j$	1.39	0.69	0.69	0	

These are points plotted in Figure 15.7 (full line). The slope is -0.416 and, since $\dfrac{\varepsilon}{hc}=50\ \mathrm{cm}^{-1}$, the slope corresponds to a temperature

$$T=\frac{(50\ \mathrm{cm}^{-1})\times(2.998\times10^{10}\ \mathrm{cm\ s}^{-1})\times(6.626\times10^{-34}\ \mathrm{J\ s})}{(0.416)\times(1.381\times10^{-23}\ \mathrm{J\ K}^{-1})}$$
$$=\boxed{163\ \mathrm{K}}$$

(A better estimate, 104 K, represented by the dashed line in Figure 15.7, is found in Problem 15.18.)

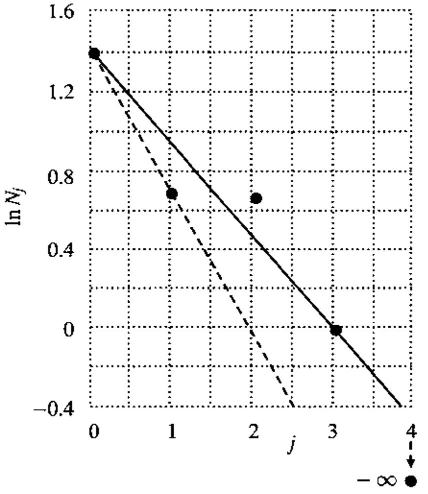


Figure 15.7

(b) Choose one of the weight 2520 configurations and one of the weight 504 configurations, and draw up the following table:

	J	0	1	2	3	4
$\mathcal{W} = 2520$	N_j	4	3	1	0	1
	$\ln N_j$	1.39	1.10	0	$-\infty$	0
$\mathcal{W} = 504$	N_j	6	0	1	1	1
	$\ln N_j$	1.79	$-\infty$	0	0	0

Inspection confirms that these data give very crooked lines.

P15.18 (a) $\langle\varepsilon\rangle = \dfrac{E(T)}{N} = -\dfrac{1}{q}\dfrac{\mathrm{d}q}{\mathrm{d}\beta}$ [15.22], with $q = \dfrac{1}{1-\mathrm{e}^{-\beta\varepsilon}}$ [15.12]

so $\langle\varepsilon\rangle = \dfrac{\varepsilon\mathrm{e}^{-\beta\varepsilon}}{1-\mathrm{e}^{-\beta\varepsilon}} = \dfrac{\varepsilon}{\mathrm{e}^{\beta\varepsilon}-1} = a\varepsilon$

Hence, $\mathrm{e}^{\beta\varepsilon} = \dfrac{1+a}{a}$, implying that $\beta = \dfrac{1}{\varepsilon}\ln\left(1+\dfrac{1}{a}\right)$

For a mean energy of ε, $a = 1$ and $\beta = \dfrac{\ln 2}{\varepsilon}$, implying that

$$T = \frac{\varepsilon}{k\ln 2} = (50\ \mathrm{cm}^{-1}) \times \left(\frac{hc}{k\ln 2}\right) = \boxed{104\ \mathrm{K}}$$

(b) $q = \dfrac{1}{1-\mathrm{e}^{-\beta\varepsilon}} = \dfrac{1}{1-\left(\dfrac{a}{1+a}\right)} = \boxed{1+a}$

P15.20 For a non-degenerate two-level system, the populations are

$$p_0 = \frac{1}{1+e^{-\beta\varepsilon}} \quad \text{and} \quad p_1 = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} \; [15.14]$$

By hypothesis, $p_1 > p_0$, so $e^{-\beta\varepsilon} > 1$, which requires $\beta < 0$ and in turn $T < 0$.

(a) The partition function is

$$q = 1 + e^{-\beta\varepsilon}$$

so the internal energy relative to that at zero temperature is

$$U(T) - U(0) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V [15.24\text{b}] = \frac{\varepsilon N e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{\varepsilon N e^{-\varepsilon/kT}}{1+e^{-\varepsilon/kT}}$$

and the entropy is

$$S(T) = \frac{U(T)-U(0)}{T} + Nk\ln q \, [15.28] = \frac{\varepsilon N e^{-\varepsilon/kT}}{T(1+e^{-\varepsilon/kT})} + Nk\ln(1+e^{-\varepsilon/kT})$$

Expressing the entropy in molar units yields

$$S_m(T) = \frac{\varepsilon R e^{-\varepsilon/kT}}{kT(1+e^{-\varepsilon/kT})} + R\ln(1+e^{-\varepsilon/kT})$$

The partition function is plotted against ε/kT in Figure 15.8(a) and against kT/ε in Figure 15.8(b). Note that the partition function is plotted on a logarithmic scale in both graphs. Notice that the partition function grows without bound as the temperature approaches zero from the negative side (i.e. as ε/kT becomes large and negative; Figure 15.8(a)). The partition function cannot really be interpreted as a count of thermally accessible states if $T < 0$.

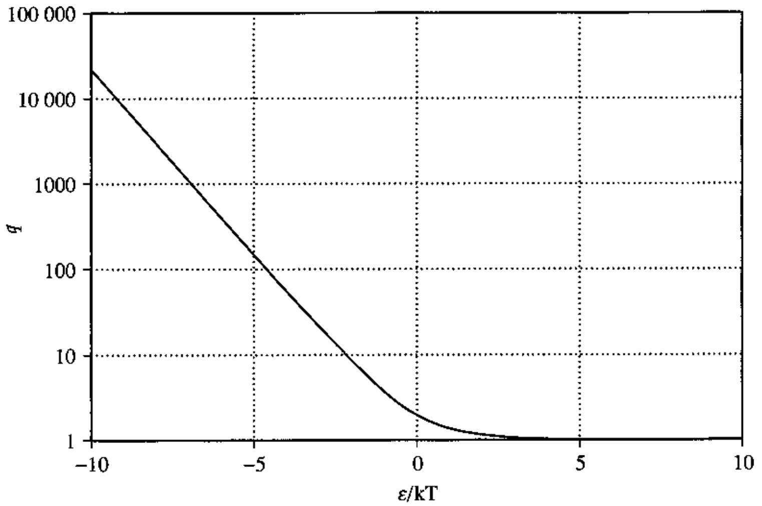


Figure 15.8(a)

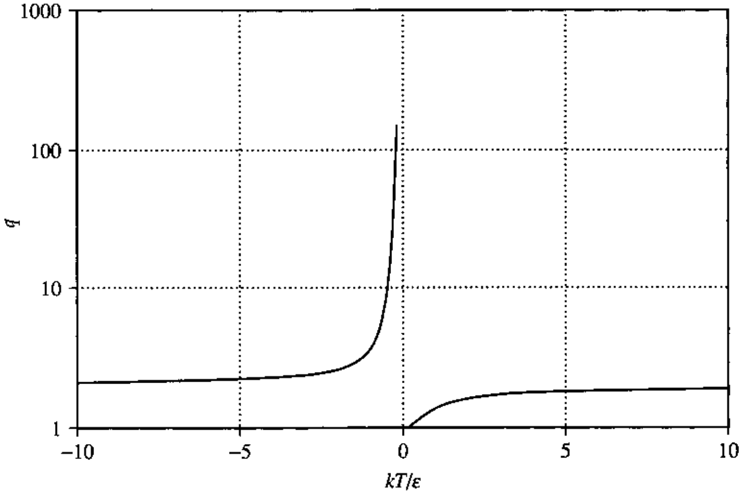


Figure 15.8(b)

Internal energy in units of $N\varepsilon$ relative to that at zero temperature and molar entropy in units of the gas constant are plotted against ε/kT in Figure 15.9(a). The same quantities are plotted against kT/ε in Figure 15.9(b).

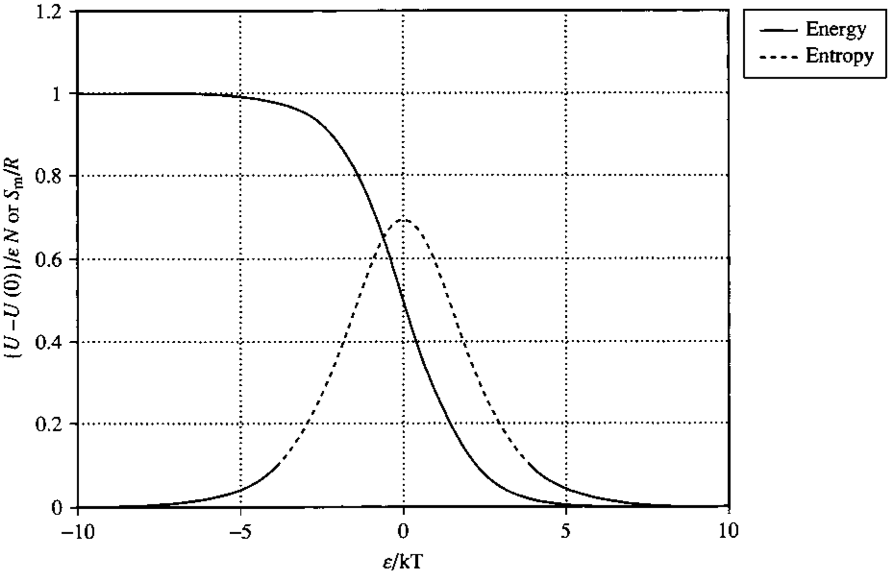


Figure 15.9(a)

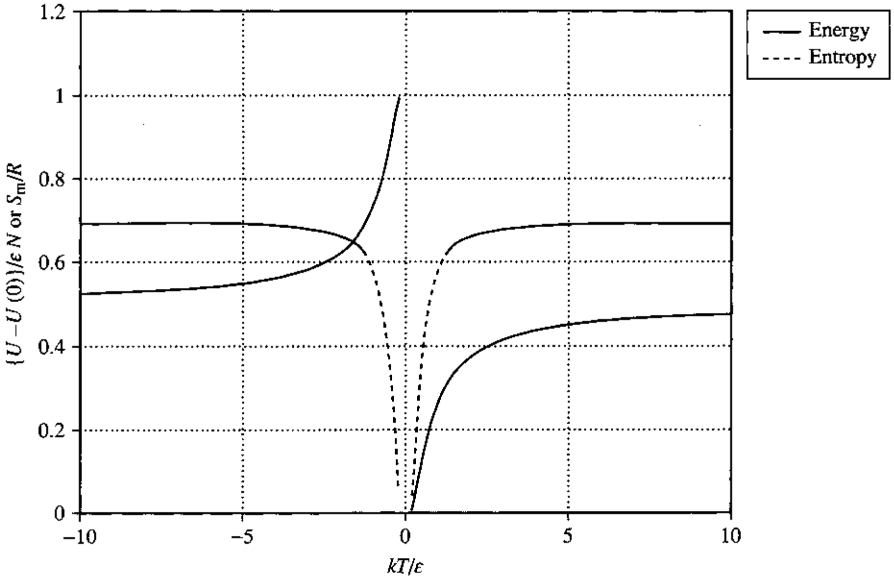


Figure 15.9(b)

Solutions to applications

P15.22 Use the perfect gas law to relate a ratio of pressures to a ratio of amounts (moles), then apply the Boltzmann distribution to the ratio of amounts:

$$\frac{p(h)}{p(h_0)} = \frac{n(h)RT/V}{n(h_0)RT/V} = \frac{n(h)}{n(h_0)} = \mathrm{e}^{-\{(\varepsilon(h)-\varepsilon(h_0))/kT\}} = \mathrm{e}^{-mg(h-h_0)/kT}$$

Defining $p(h=0) \equiv p_0$, we obtain the desired barometric formula:

$$\frac{p(h)}{p_0} = \mathrm{e}^{-mgh/kT} = \boxed{\mathrm{e}^{-Mgh/RT}} = \frac{\mathcal{N}(h)}{\mathcal{N}(0)}$$

Note that the result depends on the temperature, and it assumes that the temperature does not vary with height. To proceed, we must pick a temperature, so we use the standard temperature of 298 K, which is reasonable for the surface of the earth, but not for 8.0 km altitude.

For oxygen at 8.0 km,

$$\frac{M(\mathrm{O_2})gh}{RT} = \frac{(0.0320\ \mathrm{kg\ mol^{-1}}) \times (9.81\ \mathrm{m\ s^{-2}}) \times (8.0 \times 10^3\ \mathrm{m})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K})} \approx 1.01$$

so $$\frac{\mathcal{N}(8.0\ \mathrm{km})}{\mathcal{N}(0)} = \mathrm{e}^{-1.01} = \boxed{0.363}$$

For water,

$$\frac{M(\mathrm{H_2O})gh}{RT} = \frac{(0.0180\ \mathrm{kg\ mol^{-1}}) \times (9.81\ \mathrm{m\ s^{-2}}) \times (8.0 \times 10^3\ \mathrm{m})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K})} = 0.57$$

so $$\frac{\mathcal{N}(8.0\ \mathrm{km})}{\mathcal{N}(0)} = \mathrm{e}^{-0.57} = \boxed{0.57}$$

P15.24 (a) The electronic partition function, q^{E}, of a perfect, atomic hydrogen gas consists of the electronic energies E_n that can be written in the form:

$$E_n = \left(1 - \frac{1}{n^2}\right) hcR_{\mathrm{H}}, \quad n = 1, 2, 3, \ldots, \infty,$$

where we have used the state $n = 1$ as the zero of energy (in contrast to the usual zero being at infinite separation of the proton and electron). The degeneracy of each level is $g_n = 2n^2$, where the n^2 factor is the orbital degeneracy of each shell and the factor of 2 accounts for spin degeneracy.

$$q^{\mathrm{E}} = \sum_{n=1}^{\infty} g_n \mathrm{e}^{-E_n/kT} = 2\sum_{n=1}^{\infty} n^2 \mathrm{e}^{-\left(1-\frac{1}{n^2}\right)C}$$

where $C = hcR_{\mathrm{H}}/kT_{\text{photosphere}} = 27.301$. q^{E}, when written as an infinite sum, is infinitely large because $\lim\limits_{n\to\infty} n^2\mathrm{e}^{-\left(1-\frac{1}{n^2}\right)C} = \lim\limits_{n\to\infty} n^2\mathrm{e}^{-C} = \mathrm{e}^{-C} \lim\limits_{n\to\infty} n^2 = \infty$.

The inclusion of partition function terms corresponding to large n values is clearly an error.

(b) States corresponding to large n values have very large average radii and most certainly interact with other atoms, thereby blurring the distinct energy level of the state. Such interactions most likely occur during the collision between an atom in state n and an atom in the ground state $n = 1$. (Even at high temperatures, the ground state is the most probable state.) Collisional lifetime broadening is given by

$$\delta E_n = \frac{h}{2\pi\tau}[9.39] = \frac{z_n h}{2\pi}$$

where the last equality employs the collisional frequency (derived in Section 20.1(b)) rather than the collisional lifetime. The collisional frequency of the nth state of an atomic perfect gas is given by

$$z_n = \frac{\sigma_n \bar{c}_{\mathrm{rel}} p}{kT}[20.11\mathrm{b}] = \frac{2^{1/2}\sigma_n \bar{c} p}{kT}[20.9] = \frac{2^{1/2}\sigma_n \bar{c} \rho N_{\mathrm{A}}}{M_{\mathrm{H}}}$$

The mean speed is

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} = 1.106 \times 10^4 \text{ m s}^{-1}[20.7]$$

The collisional cross-section is

$$\sigma_n = \pi d^2 \,[\text{Section } 20.1(\mathrm{b})] = \pi(r_n + a_0)^2$$

From Example 9.2, the mean radius of a hydrogen atom with principal quantum number n might be surmised to be

$$r_n = \frac{3na_0}{2}$$

In fact, this is true of ns orbitals, which is good enough for this problem. So, the collisional cross-section is

$$\sigma_n = \pi a_0^2 \left(\frac{3n+2}{2}\right)^2$$

Any quantum state within δE of the continuum of an isolated atom will have its energy blurred by collisions so as to be indistinguishable from the continuum. Only states having energies in the range

$0 \le E < E_\infty - \delta E$ will be a distinct atomic quantum state. The maximum term, $n_{\max}$, that should be retained in the partition function of a hydrogen atom is given by

$$E_{n_{\max}} = E_\infty - \delta E_{n_{\max}}$$

$$\left(1-\frac{1}{n_{\max}^2}\right)hcR_{\mathrm{H}} = hcR_{\mathrm{H}} - \frac{2^{1/2}\pi a_0^2\left(\frac{3n_{\max}+2}{2}\right)^2 \bar{c}\rho N_{\mathrm{A}} h}{2\pi M_{\mathrm{H}}}$$

with $\rho = 1.99\times10^{-4}\,\mathrm{kg\,m^{-3}}$ and $M_{\mathrm{H}} = 1.01\times10^{-3}\,\mathrm{kg\,mol^{-1}}$. Subtracting hcR_{H} from both sides simplifies to

$$\frac{hcR_{\mathrm{H}}}{n_{\max}^2} = \frac{a_0^2\left(\frac{3n_{\max}+2}{2}\right)^2 \bar{c}\rho N_{\mathrm{A}} h}{2^{1/2} M_{\mathrm{H}}}$$

The root function of a calculator or mathematical software may be used to solve this equation for $n_{\max}$:

$\boxed{n_{\max} = 154}$ for atomic hydrogen of the photosphere

Furthermore, examination of the partition function terms $n = 2, 3, \ldots, n_{\max}$ indicates that they are negligibly small and may be discarded. The point is that very large n values should not be included in q^{E} because they do not reflect reality.

(c) The equilibrium probability of finding a hydrogen atom in energy level n is

$$p_n = \frac{2n^2 e^{-E_n/kT}}{q^{\mathrm{E}}}$$

where $T = 5780$ K. (**Note:** The probability for each distinct *state* omits the factor of $2n^2$.) This function is plotted in Figure 15.10.

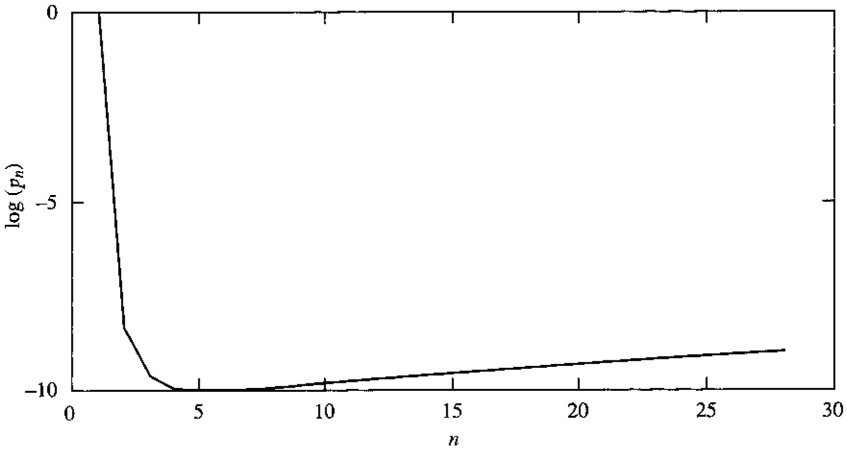


Figure 15.10

Even at the high temperature of the Sun's photosphere only the ground electronic state is significantly populated. This leads us to expect that at more ordinary temperatures only the ground state of atoms and molecules are populated at equilibrium. It would be a mistake to thoughtlessly apply equilibrium populations to a study of the Sun's photosphere, however. It is bombarded with extremely high energy radiation from the direction of the Sun's core while radiating at a much lower energy. The photosphere may show significant deviations from equilibrium. See S. J. Strickler, *J. Chem. Educ.* **43**, 364 (1966).

16

Statistical thermodynamics 2: applications

Answers to discussion questions

D16.2 The symmetry number, σ, is a correction factor to prevent the over-counting of rotational states when computing the high-temperature form of the rotational partition function. An elementary interpretation of σ is that it recognizes that in a homonuclear diatomic molecule AA the orientations AA′ and A′A are indistinguishable, and should not be counted twice, so the quantity $q = kT/hcB$ is replaced by $q = kT/\sigma hcB$ with $\sigma = 2$. A more sophisticated interpretation is that the Pauli principle allows only certain rotational states to be occupied, and the symmetry factor adjusts the high-temperature form of the partition function (which is derived by taking a sum over all states), to account for this restriction. In either case, the symmetry number is equal to the number of indistinguishable orientations of the molecule. More formally, it is equal to the order of the rotational subgroup of the molecule. (See Chapter 11.)

D16.4 The temperature is always high enough for the mean translational energy to be $\frac{3}{2}kT$, the equipartition value (provided the gas is above its condensation temperature), therefore the molar constant-volume heat capacity for translation is $C_{V,\mathrm{m}}^{\mathrm{T}} = \frac{3}{2}R$.

Translation is the only mode of motion for a monatomic gas, so for such a gas $C_{V,\mathrm{m}} = \frac{3}{2}R = 12.47$ J K^{-1} mol^{-1}. This result is very reliable: helium, for example has this value over a range of 2000 K.

When the temperature is high enough for the rotations of the molecules to be highly excited (when $T \gg \theta_{\mathrm{R}}$), we can use the equipartition value kT for the mean rotational energy (for a linear rotor) to obtain $C_{V,\mathrm{m}} = R$. For non-linear molecules, the mean rotational energy rises to $\frac{3}{2}kT$, so the molar rotational heat capacity rises to $\frac{3}{2}R$ when $T \gg \theta_{\mathrm{R}}$. Only the lowest rotational state is occupied when the temperature is very low, and then rotation does not contribute to the heat capacity. We can calculate the rotational heat capacity at intermediate temperatures by differentiating the equation for the mean rotational energy (eqn 16.26a for a linear molecule). The resulting expression is plotted in Figure 16.9 of the text. Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ($C_{V,\mathrm{m}}^{\mathrm{T}} + C_{V,\mathrm{m}}^{\mathrm{R}}$) to change from $\frac{3}{2}R$ to $\frac{5}{2}R$ as the temperature is increased above θ_{R}.

Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. For each vibrational mode, the equipartition mean energy is kT, so the maximum contribution to the molar heat capacity is R. However, it is very unusual for the vibrations to be so highly excited that equipartition is valid, and it is more appropriate to use the full expression for the vibrational heat capacity, which is obtained by differentiating eqn 16.28.

The curve in Figure 16.11 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 16.12 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_R^* (so for most molecules at normal temperatures $\nu_R^* = 2$ for linear molecules, and 3 for non-linear molecules), then the rotational contribution is $\frac{1}{2}\nu_R^* R$. If the temperature is high enough for ν_V^* vibrational modes to be active the vibrational contribution to the molar heat capacity is $\nu_R^* R$. In most cases $\nu_v \approx 0$. It follows that the total molar heat capacity is

$$C_{V,m} = \tfrac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

D16.6 The expressions for q, U, and S that were derived in this chapter are applicable to $T < 0$ as well as $T > 0$. However, if we plot q and U against T, for example, in a two-level system and other systems as well, we find sharp discontinuities on passing through zero, and $T = +0$ (corresponding to all populations in the lower state) is quite distinct from $T = -0$, where all population is in the upper state. The entropy S is continuous at $T = 0$, but all these functions are continuous if we use $\beta = 1/kT$ as the independent variable that indicates that $\beta \propto 1/T$ is a more natural variable than T. (See *Further information* 16.3 in the 8th edition of this text for a more complete discussion.)

Solutions to exercises

E16.1(b) The thermal wavelength is given by $\Lambda = \dfrac{h}{(2\pi mkT)^{1/2}}$ [15.19, 16.12]. When numerical values for h, k, and π are substituted in this expression it becomes

$$\Lambda/\text{pm} = \frac{1749}{(T/\text{K})^{1/2}(M/\text{g mol}^{-1})^{1/2}}$$

At 298.15 K, with $M = 64.06\ \text{g mol}^{-1}$ for SO_2, we obtain

$$\Lambda = \frac{1749}{(298.15 \times 64.06)^{1/2}}\ \text{pm} = \boxed{12.66\ \text{pm}} = 12.66 \times 10^{-12}\ \text{m}$$

E16.2(b) See Exercise 16.1(b).

$$q^{\text{T}} = \frac{V}{\Lambda^3}[16.12] = \frac{1.0\ \text{cm}^3 \times \dfrac{1\ \text{m}^3}{10^6\ \text{cm}^3}}{(12.66 \times 10^{-12}\ \text{m})^3} = \boxed{4.9 \times 10^{26}}$$

E16.3(b) $C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$ [16.35]

with a mode active if $T > \theta_M$.

(a) O_3: $C_{V,m} = \frac{1}{2}(3+3+0)R = 3R$ [experimental = $3.7R$]

(b) C_2H_6: $C_{V,m} = \frac{1}{2}(3+3+2\times 1)R = 4R$ [experimental = $6.3R$]

(c) CO_2: $C_{V,m} = \frac{1}{2}(3+2+0)R = \frac{5}{2}R$ [experimental ≈ $4.5R$]

Consultation of the book Herzberg (*Molecular Spectra and Molecular Structure II*) turns up only one vibrational mode among these molecules whose frequency is low enough to have a vibrational temperature near room temperature. That mode was in C_2H_6, corresponding to the 'internal rotation' of CH_3 groups. The discrepancies between the estimates and the experimental values suggest that there are vibrational modes in each molecule that contribute to the heat capacity—albeit not to the full equipartition value—that our estimates have classified as inactive.

E16.4(b) The rotational temperature is given by

$$\theta_R = \frac{hc\tilde{B}}{k} \text{ [Section 16.2(b)]}, \frac{hc}{k} = 1.4388 \text{ cm K}, \theta_R = 1.4388 \text{ cm K} \times \tilde{B}$$

For $^1H_2$: $\theta_R = 1.4388 \text{ cm K} \times 80.864 \text{ cm}^{-1} = \boxed{116.35 \text{ K}}$

For $^2H_2$: $\theta_R = 1.4388 \text{ cm K} \times 30.442 \text{ cm}^{-1} = \boxed{43.80 \text{ K}}$

E16.5(b) The rotational partition function of a linear molecule at high temperature (298 K) is (see Section 16.2(b))

$$q^R = \frac{kT}{\sigma hc\tilde{B}} = \frac{T}{\sigma\theta_R} \quad \theta_R = \frac{hc\tilde{B}}{k}$$

Substituting values for the constants this may also be written as

$$q^R = \frac{0.6950}{\sigma} \times \frac{T/\text{K}}{(\tilde{B}/\text{cm}^{-1})} = \frac{(0.6950)\times(T/\text{K})}{2\times 1.4457} = 0.2404(T/\text{K})$$

(a) At 25°C: $q^R = (0.2404)\times(298) = \boxed{71.6}$

(b) At 250°C: $q^R = (0.2404)\times(523) = \boxed{126}$

E16.6(b) The symmetry number is the order of the rotational subgroup of the group to which a molecule belongs (except for linear molecules, for which $\sigma = 2$ if the molecule has inversion symmetry and 1 otherwise).

(a) CO_2: full group $D_{\infty h}$; subgroup C_2; hence $\sigma = \boxed{2}$

(b) O_3: full group C_{2v}; subgroup C_2; $\sigma = \boxed{2}$

(c) SO_3: full group D_{3h}; subgroup $\{E, C_3, C_3^2, 3C_2\}$; $\sigma = \boxed{6}$

(d) SF_6: full group O_h; subgroup O; $\sigma = \boxed{24}$

(e) Al_2Cl_6: full group D_{2d}; subgroup D_2; $\sigma = \boxed{4}$

E16.7(b) For non-linear molecules at high temperature, $q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$ [Section 16.2b]

After substituting values for the constants this becomes

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3})^{1/2}} = \frac{1.0270\times 298^{3/2}}{(2)\times(2.02736\times 0.34417\times 0.293535)^{1/2}}\ [\sigma = 2] = \boxed{5837}$$

The high-temperature approximation is valid if $T > \theta_{\mathrm{R}}$, where

$$\theta_{\mathrm{R}} = \frac{hc(\tilde{A}\tilde{B}\tilde{C})^{1/3}}{k}$$

$$= \frac{(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times[2.02736\times0.34417\times0.293535\ \mathrm{cm}^{-3}]^{1/3}}{1.38\times10^{-23}\ \mathrm{J\ K^{-1}}}$$

$$= \boxed{0.8479\ \mathrm{K}}$$

The high-temperature approximation is clearly valid.

E16.8(b) $q^{\mathrm{R}} = 5837$ [Exercise 16.7(b)]

All rotational modes of SO_2 are active at 25°C, therefore

$$U^{\mathrm{R}}_{\mathrm{m}} - U^{\mathrm{R}}_{\mathrm{m}}(0) = E^{\mathrm{R}} = \tfrac{3}{2}RT$$

$$S^{\mathrm{R}}_{\mathrm{m}} = \frac{E^{\mathrm{R}}}{T} + R\ln q^{\mathrm{R}} = \tfrac{3}{2}R + R\ln(5837) = \boxed{84.57\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

E16.9(b) (a) The partition function is

$$q = \sum_{\text{states}} \mathrm{e}^{-E_{\text{state}}/kT} = \sum_{\text{levels}} g\mathrm{e}^{-E_{\text{level}}/kT}$$

where g is the degeneracy of the level. For rotations of a symmetric rotor such as CH_3CN, the energy levels are $E_J = hc[\tilde{B}J(J+1) + (\tilde{A}-\tilde{B})K^2]$ and the degeneracies are $g_{J,K} = 2(2J+1)$ if $K \neq 0$ and $2J+1$ if $K = 0$. The partition function, then, is

$$q = 1 + \sum_{J=1}^{\infty}(2J+1)\mathrm{e}^{-\{hc\tilde{B}J(J+1)/kT\}}\left(1 + 2\sum_{K=1}^{J}\mathrm{e}^{-\{hc(\tilde{A}-\tilde{B})K^2/kT\}}\right)$$

To evaluate this sum explicitly, we set up the following columns in a spreadsheet (values for $\tilde{A} = 5.28\ \mathrm{cm}^{-1}$, $\tilde{B} = 0.307\ \mathrm{cm}^{-1}$, and $T = 298.15$ K)

J	$J(J+1)$	$2J+1$	$\mathrm{e}^{-hc\tilde{B}J(J+1)/kT}$	J term	$\mathrm{e}^{-\{hc(\tilde{A}-\tilde{B})K^2/kT\}}$	K sum	J sum
0	0	1	1	1	1	1	1
1	2	3	0.997	8.832	0.976	2.953	9.832
2	6	5	0.991	23.64	0.908	4.770	33.47
3	12	7	0.982	43.88	0.808	6.381	77.35
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
82	6806	165	4.18×10^{-5}	0.079	8×10^{-71}	11.442	7498.95
83	6972	167	3.27×10^{-5}	0.062	2×10^{-72}	11.442	7499.01

The column labelled K sum is the term in large parentheses, which includes the inner summation. The J sum converges (to four significant figures) only at about $J = 80$; the K sum converges much more quickly, but the sum fails to take into account nuclear statistics, so it must be divided by the symmetry number ($\sigma = 3$). At 298 K, $q^{\mathrm{R}} = \boxed{2.50 \times 10^3}$. A similar computation at $T = 500$ K yields $q^{\mathrm{R}} = \boxed{5.43 \times 10^3}$.

(b) The rotational partition function of a non-linear molecule is

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$$

After substituting the values of the constants this becomes [with $\tilde{B} = \tilde{C}$]

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3})^{1/2}} = \frac{1.0270}{3}\frac{(T/\mathrm{K})^{3/2}}{(5.28 \times 0.307 \times 0.307)^{1/2}} = 0.485 \times (T/\mathrm{K})^{3/2}$$

At 298 K, $q = 0.485 \times 298^{3/2} = \boxed{2.50 \times 10^3}$

At 500 K, $q = 0.485 \times 500^{3/2} = \boxed{5.43 \times 10^3}$

The high-temperature approximation is certainly valid here.

E16.10(b) The rotational partition function of a non-linear molecule at high temperatures is (see the solution to E16.9(b) above)

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3})^{1/2}} = \frac{1.0270 \times (T/\mathrm{K})^{3/2}}{(3.1752 \times 0.3951 \times 0.3505)^{1/2}} = 1.549 \times (T/\mathrm{K})^{3/2}$$

(a) At 25°C, $q^{\mathrm{R}} = 1.549 \times (298)^{3/2} = \boxed{7.97 \times 10^3}$

(b) At 100°C, $q^{\mathrm{R}} = 1.549 \times (373)^{3/2} = \boxed{1.12 \times 10^4}$

E16.11(b) The equipartition theorem would predict a contribution to molar heat capacity of $\frac{1}{2}R$ for every translational and rotational degree of freedom and R for each vibrational mode. For an ideal gas, $C_{p,\mathrm{m}} = R + C_{V,\mathrm{m}}$. So, for CO_2

with vibrations $C_{V,\mathrm{m}}/R = 3(\frac{1}{2}) + 2(\frac{1}{2}) + (3 \times 3 - 6) = 5.5$ and $\gamma = \frac{6.5}{5.5} = \boxed{1.18}$

without vibrations $C_{V,\mathrm{m}}/R = 3(\frac{1}{2}) + 2(\frac{1}{2}) = 2.5$ and $\gamma = \frac{3.5}{2.5} = \boxed{1.40}$

experimental $\gamma = \dfrac{37.11\ \mathrm{J\ mol^{-1}\ K^{-1}}}{(37.11 - 8.3145)\ \mathrm{J\ mol^{-1}\ K^{-1}}} = \boxed{1.29}$

The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely.

E16.12(b) The molar entropy of a collection of oscillators is given by

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + k \ln Q\ [16.1] = \frac{N_{\mathrm{A}}\langle\varepsilon\rangle}{T} + R \ln q$$

where $\langle\varepsilon\rangle = \dfrac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1} = k\dfrac{\theta_V}{e^{\theta_V/T}-1}$ [16.28], $q = \dfrac{1}{1-e^{-\beta hc\tilde{\nu}}} = \dfrac{1}{1-e^{-\theta_V/T}}$ [16.19]

and θ_V is the vibrational temperature $hc\tilde{\nu}/k$. Thus,

$$S_m = \frac{R(\theta_V/T)}{e^{\theta_V/T}-1} - R\ln(1-e^{-\theta_V/T})$$

A plot of S_m/R versus T/θ_V is shown in Figure 16.1.

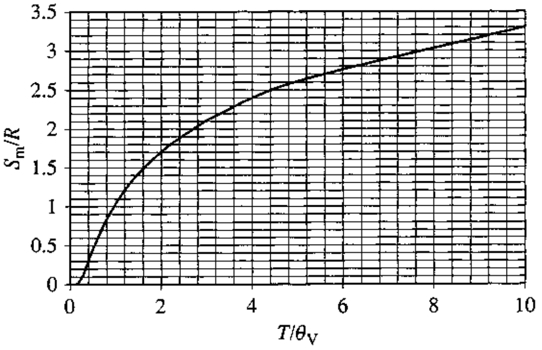


Figure 16.1

The vibrational entropy of ethyne is the sum of contributions of this form from each of its seven normal modes. The table below shows results from a spreadsheet programmed to compute S_m/R at a given temperature for the normal-mode wavenumbers of ethyne.

		$T = 298$ K		$T = 500$ K	
$\tilde{\nu}$/cm^{-1}	θ_V/K	T/θ_V	S_m/R	T/θ_V	S_m/R
612	880	0.336	0.216	0.568	0.554
729	1049	0.284	0.138	0.479	0.425
1974	2839	0.105	0.000766	0.176	0.0229
3287	4728	0.0630	0.00000217	0.106	0.000818
3374	4853	0.0614	0.00000146	0.103	0.000652

The total vibrational entropy is obtained by summing the last column (twice for the first two entries, since they represent doubly degenerate modes).

(a) At 298 K, $S_m = 0.708R = \boxed{5.88\ \mathrm{J\ mol^{-1}\ K^{-1}}}$

(b) At 500 K, $S_m = 1.982R = \boxed{16.48\ \mathrm{J\ mol^{-1}\ K^{-1}}}$

E16.13(b) The contributions of rotational and vibrational modes of motion to the molar Gibbs energy depend on the molecular partition functions

$G_m - G_m(0) = -RT\ln q$ [16.9; also see Comment to Exercise 16.8(a)]

The rotational partition function of a non-linear molecule is given by

$$q^{\mathrm{R}}=\frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}=\frac{1.0270}{\sigma}\left(\frac{(T/\mathrm{K})^3}{\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3}}\right)^{1/2}$$

and the vibrational partition function for each vibrational mode is given by

$$q^{\mathrm{V}}=\frac{1}{1-\mathrm{e}^{-\theta_{\mathrm{V}}/T}},\quad \text{where}\quad \theta_{\mathrm{V}}=\frac{hc\tilde{\nu}}{k}=1.4388\ \mathrm{K}\times(\tilde{\nu}/\mathrm{cm}^{-1})$$

At 298 K $q^{\mathrm{R}}=\dfrac{1.0270}{2}\left(\dfrac{298^3}{(3.553)\times(0.4452)\times(0.3948)}\right)^{1/2}=3.35\times10^3$

and $G_{\mathrm{m}}^{\mathrm{R}}-G_{\mathrm{m}}^{\mathrm{R}}(0)=-(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(298\ \mathrm{K})\ln 3.35\times10^3$

$$=-20.1\times10^3\ \mathrm{J\ mol^{-1}}=\boxed{-20.1\ \mathrm{kJ\ mol^{-1}}}$$

The vibrational partition functions are so small that we are better off taking

$$\ln q^{\mathrm{V}}=-\ln(1-\mathrm{e}^{-\theta_{\mathrm{V}}/T})\approx \mathrm{e}^{-\theta_{\mathrm{V}}/T}$$

$$\ln q_1^{\mathrm{V}}\approx \mathrm{e}^{-\{1.4388(1110)/298\}}=4.70\times10^{-3}$$

$$\ln q_2^{\mathrm{V}}\approx \mathrm{e}^{-\{1.4388(705)/298\}}=3.32\times10^{-2}$$

$$\ln q_3^{\mathrm{V}}\approx \mathrm{e}^{-\{1.4388(1042)/298\}}=6.53\times10^{-3}$$

so $G_{\mathrm{m}}^{\mathrm{V}}-G_{\mathrm{m}}^{\mathrm{V}}(0)=-(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(298\ \mathrm{K})\times(4.70\times10^{-3}+3.32\times10^{-2}+6.53\times10^{-3})$

$$=-110\ \mathrm{J\,mol^{-1}}=\boxed{-0.110\ \mathrm{kJ\ mol^{-1}}}$$

E16.14(b) $q=\sum_j g_j\mathrm{e}^{-\beta\varepsilon_j}$, where $g=(2S+1)\times\begin{cases}1 \text{ for } \Sigma \text{ states}\\ 2 \text{ for } \Pi, \Delta, \ldots \text{ states}\end{cases}$

The $^3\Sigma$ term is triply degenerate (from spin), and the $^1\Delta$ term is doubly (orbitally) degenerate. Hence,

$$q=3+2\mathrm{e}^{-\beta\varepsilon}$$

(a) At 500 K

$$\beta\varepsilon=\frac{(1.4388\ \mathrm{cm\ K})\times(7918.1\ \mathrm{cm^{-1}})}{500\ \mathrm{K}}=22.78$$

and $\boxed{q=3.000}$

(b) At 900 K

$$\beta\varepsilon=\frac{(1.4388\ \mathrm{cm\ K})\times(7918.1\ \mathrm{cm^{-1}})}{900\ \mathrm{K}}=12.66$$

and $\boxed{q=3.000}$

E16.15(b) See the solution to Exercise 16.14(b). $q = 3 + 2e^{-\beta\varepsilon}$

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = \frac{2N\varepsilon e^{-\beta\varepsilon}}{3 + 2e^{-\beta\varepsilon}}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -k\beta^2\left(\frac{\partial U}{\partial \beta}\right)_V = \frac{6R(\varepsilon\beta)^2 e^{-\beta\varepsilon}}{(3 + 2e^{-\beta\varepsilon})^2}[N = N_A]$$

Therefore, since at 400 K $\beta\varepsilon = 28.48$,

$$C_{V,m}/R = \frac{(6) \times (28.48)^2 \times (e^{-28.48})}{(3 + 2e^{-28.48})^2} = \boxed{2.32 \times 10^{-10}}$$

COMMENT. The electronic contribution is negligible at this temperature.

E16.16(b) See the solution to Exercise 16.14(b). At 400 K

$$\beta\varepsilon = \frac{(1.4388\ \text{cm K}) \times (7918.1\ \text{cm}^{-1})}{400\ \text{K}} = 28.48$$

Therefore, the contribution to G_m is

$G_m - G_m(0) = -RT \ln q$ [16.9, also see the Comment to Exercise 16.8(a)]

$$-RT \ln q = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K}) \times \ln(3 + 2 \times e^{-28.48})$$

$$= -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K}) \times (\ln 3) = \boxed{-3.65\ \text{kJ mol}^{-1}}$$

COMMENT. The contribution of the excited state is negligible at this temperature.

E16.17(b) The degeneracy of a species with $S = \frac{5}{2}$ is 6. The electronic contribution to molar entropy is

$$S_m = \frac{U_m - U_m(0)}{T} + R\ln q = R\ln q$$

(The term involving the internal energy is proportional to a temperature derivative of the partition function, which in turn depends on excited-state contributions to the partition function; those contributions are negligible.)

$$S_m = (8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})\ln 6 = \boxed{14.9\ \text{J mol}^{-1}\ \text{K}^{-1}}$$

E16.18(b) The Mayer *f*-function is $f = e^{-\beta E_p} - 1$. For the Lennard-Jones type [Section 17.6] of intermolecular potential of this exercise, namely $E_p = -\varepsilon\left(\frac{\sigma^6}{r^6} - \frac{\sigma^{12}}{r^{12}}\right)$, we have:

$$\begin{array}{llllll} r = 0 & E_p = \infty & f = -1 & r < \sigma & E_p > 0 & f < 0 \\ r = \sigma & E_p = 0 & f = 0 & r > \sigma & E_p < 0 & f > 0 \\ r = \infty & E_p = 0 & f = 0 & & & \end{array}$$

The general shape of the *f*-function as a function of *r* can be visualized from these relationships. The potential energy is at a minimum at $r = 2^{1/6}\sigma$ [Section 17.6] and *f* reaches its maximum at that value of *r*. In order to plot the *f*-function against *r*, we define $x = r/\sigma$ and then we write

$$E_p = -\varepsilon\left(\frac{1}{x^6} - \frac{1}{x^{12}}\right)$$

and

$$f = e^{\beta\varepsilon\left(\frac{1}{x^6} - \frac{1}{x^{12}}\right)} - 1$$

Let us assume that $\varepsilon \approx \dfrac{1}{\beta} = kT$ or some multiple of kT. Define $b = \beta\varepsilon$. Then,

$$f(x,b) = e^{b\left(\frac{1}{x^6} - \frac{1}{x^{12}}\right)} - 1$$

Now, we can plot $f(x,b)$ against x for various values of b. See Figure 16.2, in which $f(x,b)$ is plotted for $b = 1$, 2, and 3.

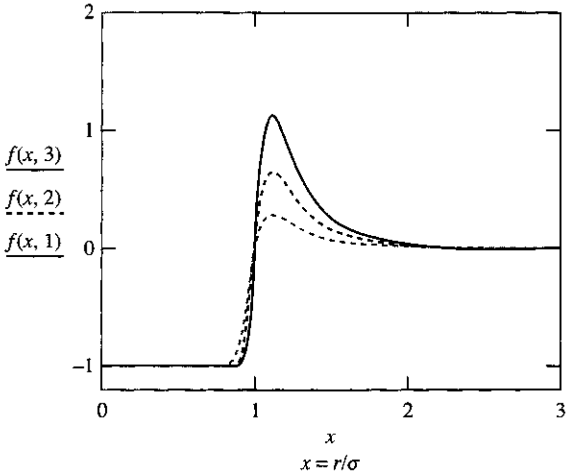


Figure 16.2

E16.19(b) Use $S_m = R \ln s$ [16.50b]

Draw up the following table:

n:	0	1	2			3			4			5	6
			o	m	p	a	b	c	o	m	p		
s	1	6	6	6	3	6	6	2	6	6	3	6	1
S_m/R	0	1.8	1.8	1.8	1.1	1.8	1.8	0.7	1.8	1.8	1.1	1.8	0

where a is the 1, 2, 3 isomer, b is the 1, 2, 4 isomer, and c is the 1, 3, 5 isomer.

E16.20(b) We need to calculate

$$K = \prod_J \left(\frac{q^{\ominus}_{J,m}}{N_A}\right)^{\nu_J} \times e^{-\Delta_r E_0/RT} \text{ [16.52b]} = \frac{q^{\ominus}_m({}^{79}\mathrm{Br}_2)\,q^{\ominus}_m({}^{81}\mathrm{Br}_2)}{q^{\ominus}_m({}^{79}\mathrm{Br}{}^{81}\mathrm{Br})^2}\,e^{-\Delta_r E_0/RT}$$

Each of these partition functions is a product

$$q_m^{\ominus} = q_m^T q^R q^V q^E$$

with all $q^E = 1$.

The ratio of the translational partition functions is virtually 1 (because the masses nearly cancel; explicit calculation gives 0.999). The same is true of the vibrational partition functions. Although the moments of inertia cancel in the rotational partition functions, the two homonuclear species each have $\sigma = 2$, so

$$\frac{q^R(^{79}\mathrm{Br}_2)q^R(^{81}\mathrm{Br}_2)}{q^R(^{79}\mathrm{Br}^{81}\mathrm{Br})^2} = 0.25$$

The value of $\Delta_r E_0$ is also very small compared with RT, so

$$K \approx \boxed{0.25}$$

Solutions to problems

Solutions to numerical problems

P16.2

$$\Delta\varepsilon = \varepsilon = g\mu_B \mathcal{B}_0 \; [14.39]$$

$$q = 1 + e^{-\beta\varepsilon}$$

$$C_{V,m}/R = \frac{x^2 e^{-x}}{(1+e^{-x})^2} \text{ [Problem 16.1]}, \quad x = 2\mu_B\mathcal{B}_0\beta \text{ [}g = 2 \text{ for electrons]}$$

Therefore, if $\mathcal{B}_0 = 5.0$ T,

$$x = \frac{(2)\times(9.274\times10^{-24}\ \mathrm{J\ T^{-1}})\times(5.0\ \mathrm{T})}{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times T} = \frac{6.72}{T/\mathrm{K}}$$

(a) $T = 50$ K, $x = 0.134$, $C_V = 4.47 \times 10^{-3}R$, implying that $C_V = 3.7 \times 10^{-2}$ J K^{-1} mol^{-1}. Since the equipartition value is about $3R$ [$\nu_R^* = 3$, $\nu_V^* \approx 0$], the field brings about a change of about $\boxed{0.1\%}$

(b) $T = 298$ K, $x = 2.26 \times 10^{-2}$, $C_V = 1.3 \times 10^{-4}R$, implying that $C_V = 1.1$ mJ K^{-1} mol^{-1}, a change of about $\boxed{4\times10^{-3}\%}$

Question. What percentage change would a magnetic field of 1 kT cause?

P16.4

$$q = 1 + 5e^{-\beta\varepsilon} \quad [g_J = 2J+1]$$

$$\varepsilon = E(J=2) - E(J=0) = 6hc\tilde{B} \quad [E = hc\tilde{B}J(J+1)]$$

$$\frac{U - U(0)}{N} = -\frac{1}{q}\frac{\partial q}{\partial \beta} = \frac{5\varepsilon e^{-\beta\varepsilon}}{1+5e^{-\beta\varepsilon}}$$

$$C_{V,m} = -k\beta^2\left(\frac{\partial U_m}{\partial \beta}\right)_V \; [16.31a]$$

$$C_{V,\mathrm{m}}/R=\frac{5\varepsilon^2\beta^2\mathrm{e}^{-\beta\varepsilon}}{(1+5\mathrm{e}^{-\beta\varepsilon})^2}=\frac{180(hc\tilde{B}\beta)^2\mathrm{e}^{-6hc\tilde{B}\beta}}{(1+5\mathrm{e}^{-6hc\tilde{B}\beta})^2}$$

$$\frac{hc\tilde{B}}{k}=1.4388\ \mathrm{cm\ K}\ \times 60.864\ \mathrm{cm}^{-1}=87.571\ \mathrm{K}$$

Hence,

$$C_{V,\mathrm{m}}/R=\frac{1.380\times 10^6\ \mathrm{e}^{-525.4\ \mathrm{K}/T}}{(1+5\mathrm{e}^{-525.4\ \mathrm{K}/T})^2\times(T/\mathrm{K})^2}$$

We draw up the following table:

T/K	50	100	150	200	250	300	350	400	450	500
$C_{V,\mathrm{m}}/R$	0.02	0.68	1.40	1.35	1.04	0.76	0.56	0.42	0.32	0.26

These points are plotted in Figure 16.3.

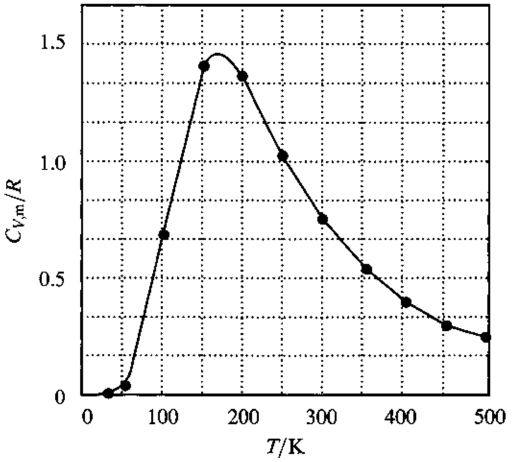


Figure 16.3

P16.6

$$\frac{q_\mathrm{m}^{T\ominus}}{N_\mathrm{A}}=\frac{kT}{p^\ominus\Lambda^3}\qquad \Lambda=\frac{h}{(2\pi mkT)^{1/2}}$$

After substituting values for the constants we obtain

$$\frac{q_\mathrm{m}^{T\ominus}}{N_\mathrm{A}}=2.561\times10^{-2}\times(T/\mathrm{K})^{5/2}\times(M/\mathrm{g\ mol}^{-1})$$

$$=(2.561\times10^{-2})\times(298)^{5/2}\times(28.02)^{3/2}=5.823\times10^6$$

$$q^\mathrm{R}=\frac{kT}{\sigma hc\tilde{B}}=\frac{T}{\sigma\theta_\mathrm{R}}\qquad \theta_\mathrm{R}=\frac{hc\tilde{B}}{k}$$

After substituting values for the constants we obtain

$$q^\mathrm{R}=\frac{0.6950}{\sigma}\times\frac{T/\mathrm{K}}{(\tilde{B}/\mathrm{cm}^{-1})}=\frac{0.6950}{2}\times\frac{298}{1.9987}=51.81$$

$$q^{\mathrm{V}}=\frac{1}{1-\mathrm{e}^{-\theta_{\mathrm{V}}/T}}$$

where $\theta_{\mathrm{V}}=\frac{hc\tilde{\nu}}{k}=\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times2.998\times10^{10}\,\mathrm{cm\,s^{-1}}\times2358\,\mathrm{cm^{-1}}}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}}=3392\,\mathrm{K}$

so $q^{\mathrm{V}}=\frac{1}{1-\mathrm{e}^{-3392\,\mathrm{K}/298\,\mathrm{K}}}=1.00$

Therefore,

$$\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}}=(5.82\bar{3}\times10^{6})\times(51.8\bar{1})\times(1.00)=3.02\times10^{8}$$

$$U_{\mathrm{m}}-U_{\mathrm{m}}(0)=\tfrac{3}{2}RT+RT=\tfrac{5}{2}RT\quad[T\gg\theta_{\mathrm{T}},\theta_{\mathrm{R}}]$$

Hence,

$$S_{\mathrm{m}}^{\ominus}=\frac{U_{\mathrm{m}}-U_{\mathrm{m}}(0)}{T}+R\left(\ln\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}}+1\right)$$

$$=\tfrac{5}{2}R+R\{\ln3.02\times10^{8}+1\}=23.03R=\boxed{191.4\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

The difference between the experimental and calculated values is negligible, indicating that the residual entropy is negligible.

P16.8 The vibrational temperature is defined by

$$k\theta_{\mathrm{V}}=hc\tilde{\nu},$$

so a vibration with θ_{V} less than 1000 K has a wavenumber less than

$$\tilde{\nu}=\frac{k\theta_{\mathrm{V}}}{hc}=\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(1000\,\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm}\,s^{-1})}=695.2\,\mathrm{cm^{-1}}$$

There are seven such wavenumbers listed among those for C_{60}: two T_{1u}, a T_{2u}, a G_{u}, and three H_{u}. The number of *modes* involved, ν_{V}^{*}, must take into account the degeneracy of these vibrational energies:

$$\nu_{\mathrm{V}}^{*}=2(3)+1(3)+1(4)+3(5)=\boxed{28}$$

The molar heat capacity of a molecule is roughly

$$C_{V,\mathrm{m}}=\tfrac{1}{2}(3+\nu_{\mathrm{R}}^{*}+2\nu_{\mathrm{V}}^{*})R\,[1.35]=\tfrac{1}{2}(3+3+2\times28)R=31R=31\,(8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})$$

$$=\boxed{258\,\mathrm{J\,mol^{-1}\,K^{-1}}}$$

P16.10 The second virial coefficient is given by $B=-2\pi N_{\mathrm{A}}\int_0^{\infty}fr^2\mathrm{d}r\,[16.42]$, where f is the Mayer f-function:

$$f=\mathrm{e}^{-\beta E_{\mathrm{P}}}-1\,[16.42]$$

The intermolecular potential given in this problem, namely $E_p = -\varepsilon\left(\frac{\sigma^6}{r^6} - \frac{\sigma^{12}}{r^{12}}\right)$, is a Lennard-Jones type [Section 17.6, eqn 17.33] of intermolecular potential. Note, however, that ε in E_p as given in the problem is four times the value of ε of eqn 17.33 and is four times the values found in Table 17.4. σ in E_p can be identified with r_0 in eqn 17.33 and Table 17.4. In order to be consistent with the standard form of the Lennard-Jones potential we prefer to add the factor of 4. Then,

$$f = \mathrm{e}^{\frac{4\varepsilon}{kT}\left(\frac{\sigma^6}{r^6} - \frac{\sigma^{12}}{r^{12}}\right)} - 1$$

Let us first solve for B in terms of dimensionless variables. We define the reduced variables $z \equiv \frac{r}{\sigma}$ and $t \equiv \frac{kT}{\varepsilon}$, and the reduced second virial coefficient $b \equiv \frac{B}{2\frac{\pi}{3}N_A\sigma^3}$. These transformations to reduced variables, which are used in the following MathCad calculation of the reduced second virial coefficient, are consistent with the definitions in Hirschfelder, Curtis, and Bird, *Molecular Theory of Gases and Liquids*, the standard reference on second virial coefficients. With these transformations eqn 16.42 becomes

$$f(t,z) := \mathrm{e}^{\frac{4(z^{-6}-z^{-12})}{t}} - 1 \qquad b(t) := -\int_0^{\infty} 3f(t,z)\cdot z^2\,dz$$

The reduced second virial coefficient is plotted against the reduced temperature in Figure 16.4(a). The values in this plot are consistent with the calculated classical curve in Figure 3.6-1 on page 164 of Hirschfelder *et al.* The plot shows the dependence of the second virial coefficient on temperature and the transformation shows that B is proportional to σ^3.

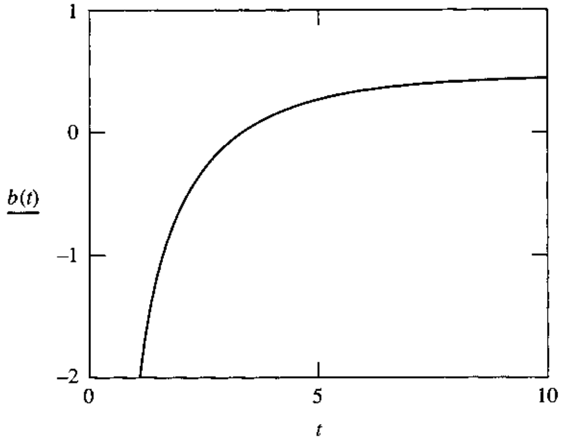


Figure 16.4(a)

We may also determine B itself for a particular gas and this is done in the following MathCad calculation for Argon. Lennard-Jones parameters are from Table 17.4.

$$\sigma := 3.623\cdot 10^{-10}\cdot \mathrm{m} \qquad k := 1.38065\cdot 10^{-23}\cdot \mathrm{J}\cdot \mathrm{K}^{-1}$$

$$i := 1, 2 .. 40 \qquad T_i := i\cdot 10\cdot \mathrm{K} \qquad \varepsilon := 4k\cdot 111.84\cdot \mathrm{K} \qquad N_A := 6.02214\cdot 10^{23}\cdot \mathrm{mol}^{-1}$$

$$f(z,i) := e^{\left(\frac{\varepsilon}{k\cdot T_i}\right)\cdot\left[\left(z^{-6}\right)-\left(z^{-12}\right)\right]} - 1 \quad B_i := -2\cdot\pi\cdot N_A\cdot\sigma^3\cdot\int_0^{\infty} f(z,i)\cdot z^2\,dz$$

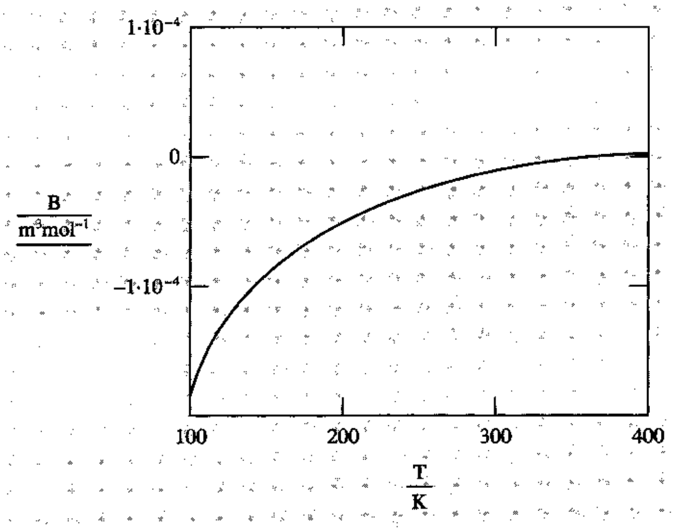


Figure 16.4(b)

Comparison of the values of B for argon in this plot with the data in Table 1.4 show a very close match. For example, the calculated value at 100 K is $-1.848\ \mathrm{m^3\ mol^{-1}}$ and the experimental value is $-1.87\ \mathrm{m^3\ mol^{-1}}$.

P16.12 $H_2O + DCl \rightleftharpoons HDO + HCl$

$$K = \frac{q^{\ominus}(\mathrm{HDO})q^{\ominus}(\mathrm{HCl})}{q^{\ominus}(\mathrm{H_2O})q^{\ominus}(\mathrm{DCl})}e^{-\beta\Delta_r E_0}$$ [16.52; with $\Delta_r E_0$ here defined as the molecular, not molar, energy difference; N_A factors cancel]

Use partition function expressions from the checklist of key equations, Chapters 15 and 16. The ratio of translational partition functions is

$$\frac{q_m^T(\mathrm{HDO})q_m^T(\mathrm{HCl})}{q_m^T(\mathrm{H_2O})q_m^T(\mathrm{DCl})} = \left(\frac{M(\mathrm{HDO})M(\mathrm{HCl})}{M(\mathrm{H_2O})M(\mathrm{DCl})}\right)^{3/2} = \left(\frac{19.02\times 36.46}{18.02\times 37.46}\right)^{3/2} = 1.041$$

The ratio of rotational partition functions is

$$\frac{q^R(\mathrm{HDO})q^R(\mathrm{HCl})}{q^R(\mathrm{H_2O})q^R(\mathrm{DCl})} = \frac{\sigma(\mathrm{H_2O})}{1}\,\frac{(\tilde{A}(\mathrm{H_2O})\tilde{B}(\mathrm{H_2O})\tilde{C}(\mathrm{H_2O})/\mathrm{cm^{-3}})^{1/2}\tilde{B}(\mathrm{DCl})/\mathrm{cm^{-1}}}{(\tilde{A}(\mathrm{HDO})\tilde{B}(\mathrm{HDO})\tilde{C}(\mathrm{HDO})/\mathrm{cm^{-3}})^{1/2}\tilde{B}(\mathrm{HCl})/\mathrm{cm^{-1}}}$$

$$= 2\times\frac{(27.88\times 14.51\times 9.29)^{1/2}\times 5.449}{(23.38\times 9.102\times 6.417)^{1/2}\times 10.59} = 1.707$$

($\sigma = 2$ for H_2O; $\sigma = 1$ for the other molecules).

The ratio of vibrational partition functions (call it Q) is

$$\frac{q^{\mathrm{V}}(\mathrm{HDO})q^{\mathrm{V}}(\mathrm{HCl})}{q^{\mathrm{V}}(\mathrm{H_2O})q^{\mathrm{V}}(\mathrm{DCl})}=\frac{q(2726.7)q(1402.2)q(3707.5)q(2991)}{q(3656.7)q(1594.8)q(3755.8)q(2145)}=Q$$

where $q(x)=\dfrac{1}{1-\mathrm{e}^{-1.4388x/(T/\mathrm{K})}}$

$$\frac{\Delta_r E_0}{hc}=\tfrac{1}{2}\{(2726.7+1402.2+3707.5+2991)-(3656.7+1594.8+3755.8+2145)\}\ \mathrm{cm^{-1}}$$
$$=-162\ \mathrm{cm^{-1}}$$

So, the exponent in the energy term is

$$-\beta\Delta_r E_0=-\frac{\Delta_r E_0}{kT}=-\frac{hc}{k}\times\frac{\Delta_r E_0}{hc}\times\frac{1}{T}=-\frac{1.4388\times(-162)}{T/\mathrm{K}}=+\frac{233}{T/\mathrm{K}}$$

Therefore, $K=1.041\times1.707\times Q\times \mathrm{e}^{233/(T/\mathrm{K})}=1.777Q\mathrm{e}^{233/(T/\mathrm{K})}$

We then draw up the following table (using a computer):

T/K	100	200	300	400	500	600	700	800	900	1000
K	18.3	5.70	3.87	3.19	2.85	2.65	2.51	2.41	2.34	2.29

and specifically $K=\boxed{3.89}$ at (a) 298 K and $\boxed{2.41}$ at (b) 800 K.

Solutions to theoretical problems

P16.14 (a) θ_{V} and θ_{R} are the constant factors in the numerators of the negative exponents in the sums that are the partition functions for vibration and rotation. They have the dimensions of temperature, which occurs in the denominator of the exponents. So high temperature means $T\gg\theta_{\mathrm{V}}$ or θ_{R} and only then does the exponential become substantial. Thus, θ_{V} and θ_{R} are measures of the temperature at which higher vibrational and rotational states, respectively, become significantly populated.

$$\theta_{\mathrm{R}}=\frac{hc\tilde{B}}{k}=\frac{(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times(6.626\times10^{-34}\ \mathrm{J\ s})\times(60.864\ \mathrm{cm^{-1}})}{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})}=\boxed{87.55\ \mathrm{K}}$$

and $$\theta_{\mathrm{V}}=\frac{hc\tilde{\nu}}{k}=\frac{(6.626\times10^{-34}\ \mathrm{J\ s})\times(4400.39\ \mathrm{cm^{-1}})\times(2.998\times10^{10}\ \mathrm{cm s^{-1}})}{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})}=\boxed{6330\ \mathrm{K}}$$

(b) and (c) These parts of the solution were performed with Mathcad and are reproduced on the following pages.

Objective: To calculate the equilibrium constant $K(T)$ and $C_p(T)$ for dihydrogen at high temperature for a system made with n mol H_2 at 1 bar.

$$\mathrm{H_2(g)}\rightleftharpoons 2\,\mathrm{H(g)}$$

At equilibrium, the degree of dissociation, α, and the equilibrium amounts of H_2 and atomic hydrogen are related by the expressions

$$n_{\mathrm{H_2}}=(1-\alpha)n \quad\text{and}\quad n_{\mathrm{H}}=2\alpha n$$

The equilibrium mole fractions are

$$x_{H_2} = (1-\alpha)n/\{(1-\alpha)n + 2\alpha n\} = (1-\alpha)/(1+\alpha)$$

$$x_H = 2\alpha n/\{(1-\alpha)n + 2\alpha n\} = 2\alpha/(1+\alpha)$$

The partial pressures are

$$p_{H_2} = (1-\alpha)p/(1+\alpha) \quad \text{and} \quad p_H = 2\alpha p/(1+\alpha)$$

The equilibrium constant is

$$K(T) = \frac{(p_H/p^\ominus)^2}{(p_{H_2}/p^\ominus)} = 4\alpha^2\frac{(p/p^\ominus)}{(1-\alpha^2)} = \frac{4\alpha^2}{(1-\alpha^2)}, \text{ where } p = p^\ominus = 1\text{ bar}$$

The above equation is easily solved for α

$$\boxed{\alpha = (K/(K+4))^{1/2}}$$

The heat capacity at constant volume for the equilibrium mixture is

$$C_V(\text{mixture}) = n_H C_{V,m}(H) + n_{H_2}C_{V,m}(H_2)$$

The heat capacity at constant volume per mole of dihydrogen used to prepare the equilibrium mixture is

$$\begin{aligned} C_V = C_V(\text{mixture})/n &= \{n_H C_{V,m}(H) + n_{H_2}C_{V,m}(H_2)\}/n \\ &= \boxed{2\alpha C_{V,m}(H) + (1-\alpha)C_{V,m}(H_2)} \end{aligned}$$

The formula for the heat capacity at constant pressure per mole of dihydrogen used to prepare the equilibrium mixture (C_p) can be deduced from the molar relationship

$$C_{p,m} = C_{V,m} + R$$

$$\begin{aligned} C_p &= \{n_H C_{p,m}(H) + n_{H_2}C_{p,m}(H_2)\}/n \\ &= \frac{n_H}{n}\{C_{V,m}(H) + R\} + \frac{n_{H_2}}{n}\{C_{V,m}(H_2) + R\} \\ &= \frac{n_H C_{V,m}(H) + n_{H_2}C_{V,m}(H_2)}{n} + R\left(\frac{n_H + n_{H_2}}{n}\right) \\ &= C_V + R(1+\alpha) \end{aligned}$$

Calculations

J = joule
mol = mole
$h = 6.62608 \times 10^{-34}$ J s
$R = 8.31451$ J K^{-1} mol^{-1}
s = second
g = gram
$c = 2.9979 \times 10^{8}$ m s^{-1}
$N_A = 6.02214 \times 10^{23}$ mol^{-1}
kJ = 1000 J
bar = 1×10^{5} Pa
$k = 1.38066 \times 10^{-23}$ J K^{-1}
$p^\ominus = 1$ bar

Molecular properties of H_2

$$\tilde{\nu} = 4400.39\text{ cm}^{-1} \quad \tilde{B} = 60.864\text{ cm}^{-1} \quad D = 432.1\text{ kJ mol}^{-1}$$

$$m_H = \frac{1\text{ g mol}^{-1}}{N_A}; \quad m_{H_2} = 2m_H$$

$$\theta_V = \frac{hc\tilde{v}}{k} \quad \theta_R = \frac{hc\tilde{B}}{k}$$

Computation of $K(T)$ and $\alpha(T)$

$$N = 200 \quad i = 0, \ldots, N \quad T_i = 500K + \frac{i \times 5500\ \mathrm{K}}{N}$$

$$\Lambda_{Hi} = \frac{h}{(2\pi m_H k T_i)^{1/2}}; \quad \Lambda_{H_2 i} = \frac{h}{(2\pi m_{H_2} k T_i)^{1/2}}$$

$$q_{Vi} = \frac{1}{1 - e^{-(\theta_V/T_i)}}; \quad q_{Ri} = \frac{T_i}{2\theta_R}$$

$$\boxed{K_{eqi} = \frac{kT_i(\Lambda_{H_2 i})^3 e^{-(D/RT_i)}}{p^{\ominus} q_{Vi} q_{Ri} (\Lambda_{Hi})^6}} \quad \alpha_i = \left(\frac{K_{eqi}}{K_{eqi} + 4}\right)^{1/2}$$

See Figures 16.5(a) and (b).

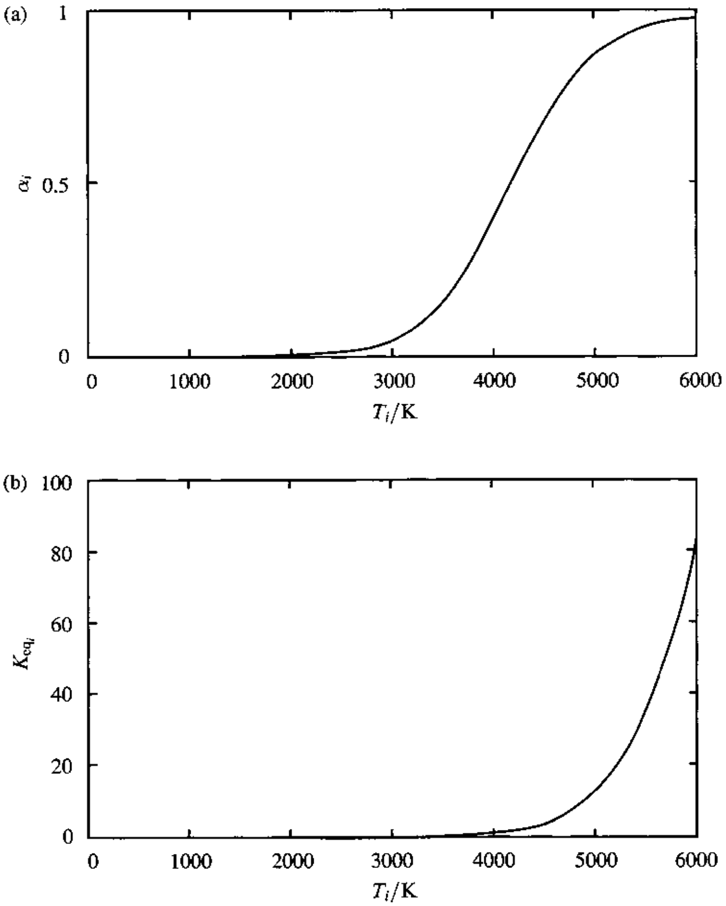


Figure 16.5(a) & (b)

Heat capacity at constant volume per mole of dihydrogen used to prepare the equilibrium mixture is (see Figure 16.6(a))

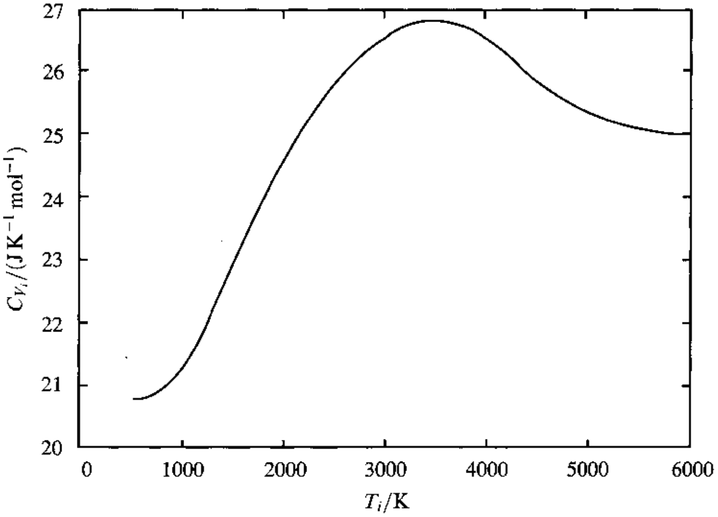


Figure 16.6(a)

$$C_V(\mathrm{H}) = \boxed{1.5R}$$

$$C_{V_i}(\mathrm{H_2}) = \boxed{2.5R + \left[\frac{\theta_\mathrm{V}}{T_i} \times \frac{\mathrm{e}^{-(\theta_\mathrm{V}/2T_i)}}{1-\mathrm{e}^{\theta_\mathrm{V}/T_i}}\right]^2 R} \quad C_{V_i} = 2\alpha_i C_V(\mathrm{H}) + (1-\alpha_i)C_V(\mathrm{H}_{2_i})$$

The heat capacity at constant pressure per mole of dihydrogen used to prepare the equilibrium mixture is (see Figure 16.6(b))

$$C_{p_i} = C_{V_i} + R(1+\alpha_i)$$

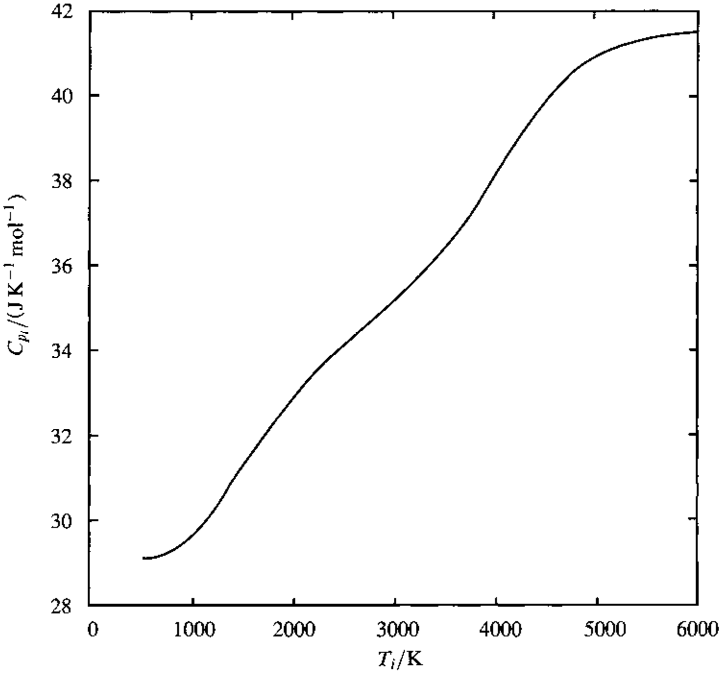


Figure 16.6(b)

P16.16 The contribution to the heat capacity from this system of states is

$$C_V = -k\beta^2\left(\frac{\partial U}{\partial \beta}\right)_V \; [16.31\text{a}] = \left(\frac{\partial U}{\partial T}\right)_V$$

where $$U - U(0) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V \; [15.24\text{a}] = \frac{NkT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V$$

We need to evaluate q for the energy levels of the Morse potential given by eqn 12.38:

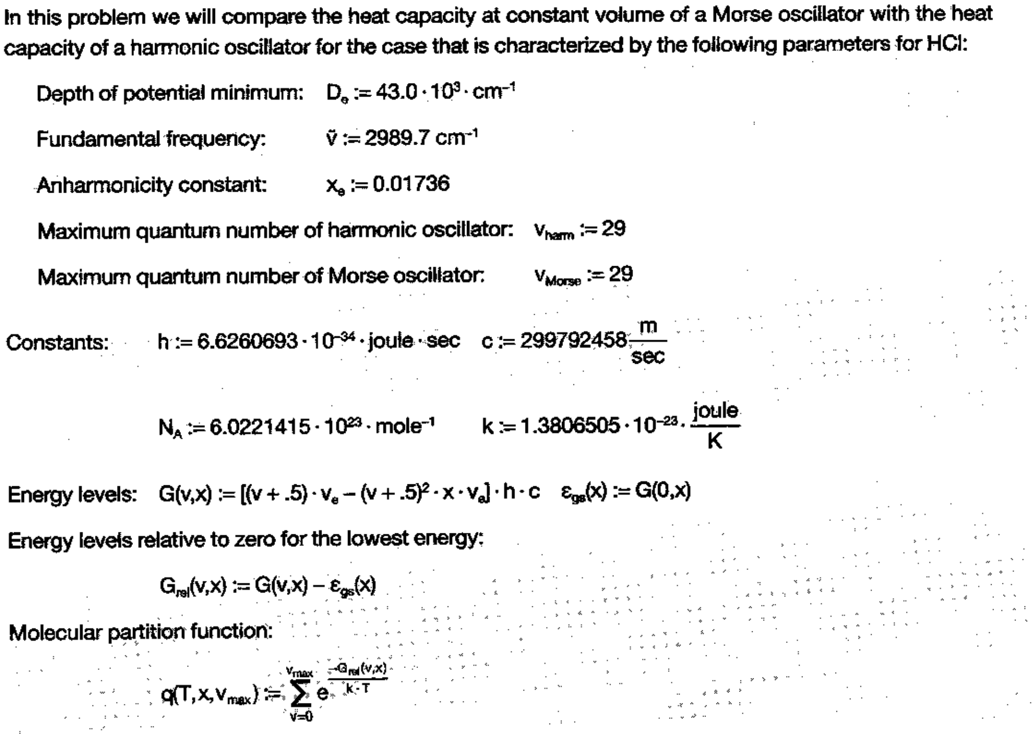
$$E_v = (v + \tfrac{1}{2})hc\tilde{\nu} - (v + \tfrac{1}{2})^2 hc\tilde{\nu}x_e \; [12.38]$$

Relative to $E_0 = 0$ the energy expression can be written as $E_v = vhc\tilde{\nu}[1 - (v + 1)x_e]$.

Let $hc\tilde{\nu} \equiv u$. Then, $E_v = uv[1 - (v + 1)x_e]$. The partition function becomes

$$q = \sum_{v=0}^{v_{\max}} e^{-\beta E_v} = \sum_{v=0}^{v_{\max}} e^{-\beta\{uv[1-(v+1)x_e]\}} = \sum_{v=0}^{v_{\max}} e^{-\{uv[1-(v+1)x_e]\}/kT}$$

$v_{\max}$ is the maximum value of v for the Morse oscillator before dissociation occurs. It can be calculated from $v_{\max} = \dfrac{2\tilde{D}_e}{\tilde{\nu}} - \dfrac{1}{2}$. See the solution to Problem 12.24 for a derivation of this formula. Since specific values of x_e, $\tilde{\nu}$, and $\tilde{D}_e$ are required to solve this problem we will choose the case of HCl(g). Values of $\tilde{D}_e$, $\tilde{\nu}$, and x_e may be obtained from Table 12.2 and Problem 12.12. The value of x_e can also be calculated from $x_e = \dfrac{\tilde{\nu}}{4\tilde{D}_e}$ [12.38]. The heat capacity is calculated in the following MathCad worksheet and Figure 16.7.



In this problem we will compare the heat capacity at constant volume of a Morse oscillator with the heat capacity of a harmonic oscillator for the case that is characterized by the following parameters for HCl:

Depth of potential minimum: $D_e := 43.0 \cdot 10^3 \cdot \text{cm}^{-1}$

Fundamental frequency: $\tilde{\nu} := 2989.7\ \text{cm}^{-1}$

Anharmonicity constant: $x_e := 0.01736$

Maximum quantum number of harmonic oscillator: $v_{\text{harm}} := 29$

Maximum quantum number of Morse oscillator: $v_{\text{Morse}} := 29$

Constants: $h := 6.6260693 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec}$ $\quad c := 299792458 \dfrac{\text{m}}{\text{sec}}$

$N_A := 6.0221415 \cdot 10^{23} \cdot \text{mole}^{-1}$ $\quad k := 1.3806505 \cdot 10^{-23} \cdot \dfrac{\text{joule}}{\text{K}}$

Energy levels: $G(v,x) := [(v + .5) \cdot v_e - (v + .5)^2 \cdot x \cdot v_e] \cdot h \cdot c$ $\quad \varepsilon_{gs}(x) := G(0,x)$

Energy levels relative to zero for the lowest energy:

$$G_{rel}(v,x) := G(v,x) - \varepsilon_{gs}(x)$$

Molecular partition function:

$$q(T,x,v_{max}) := \sum_{v=0}^{v_{max}} e^{\frac{-G_{rel}(v,x)}{k \cdot T}}$$

Mean energy [16.24]:

$$\varepsilon_{\mathrm{mean}}(T,x,v_{\mathrm{max}}) := \frac{k\cdot T^2}{q(T,x,v_{\mathrm{max}})}\cdot\left(\frac{d}{dT}q(T,x,v_{\mathrm{max}})\right)$$

$$T := 5\cdot K, 25\cdot K..2000\cdot K$$

$$C_V(T,x_e,v_{\mathrm{Morse}}) := N_A\cdot\left(\frac{d}{dT}\varepsilon_{\mathrm{mean}}(T,x_e,v_{\mathrm{Morse}})\right)$$

$$C_V(298.15\,K,x_e,v_{\mathrm{Morse}}) = 1.392\times10^{-3}\,\frac{J}{K\cdot mol}$$

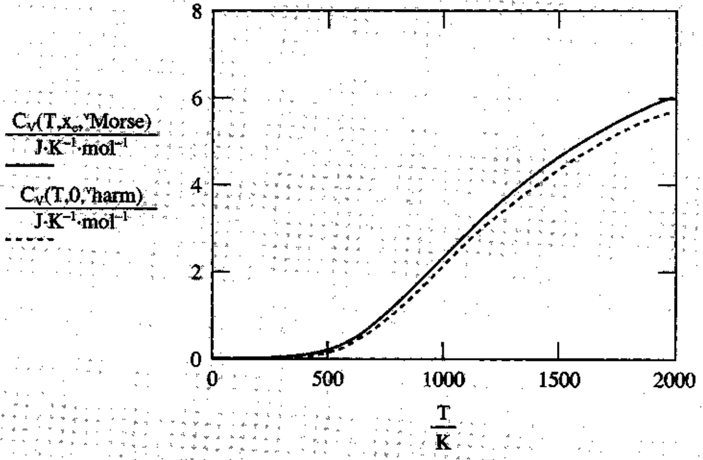


Figure 16.7

Note the slight difference between the vibrational heat capacities of the harmonic-oscillator approximation and the Morse-oscillator approximation. Also note that for HCl(g) at room temperature the vibrational energy levels make essentially no contribution to the overall heat capacity of 29.12 J K^{-1} mol^{-1}. This is a result of the large spacing between the HCl energy levels.

P16.18 (a) Ethene belongs to the D_{2h} point group, whose rotational subgroup includes E and three C_2 elements around different axes, so $\sigma = 4$. The rotational partition function of a non-linear molecule is

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$$

After substituting for the constants this becomes

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3})^{1/2}} = \frac{1.0270\times298.15^{3/2}}{(4)\times(4.828\times1.0012\times0.8282)^{1/2}} = \boxed{660.6}$$

(b) Pyridine belongs to the C_{2v} group, the same as water, so $\sigma = 2$.

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm}^{-3})^{1/2}} = \frac{1.0270\times298.15^{3/2}}{(2)\times(0.2014\times0.1936\times0.0987)^{1/2}} = \boxed{4.26\times10^4}$$

P16.20 The partition function of a system with energy levels $\varepsilon(J)$ and degeneracies $g(J)$ is

$$q=\sum_J g(J)\mathrm{e}^{-\beta\varepsilon(J)}$$

The contribution of the heat capacity from this system of states is

$$C_V=-k\beta^2\left(\frac{\partial U}{\partial\beta}\right)_V \quad [16.31\mathrm{a}]$$

where $U-U(0)=-N\left(\dfrac{\partial\ln q}{\partial\beta}\right)_V=-\dfrac{N}{q}\left(\dfrac{\partial q}{\partial\beta}\right)_V$

Express these quantities in terms of sums over energy levels

$$U-U(0)=-\frac{N}{q}\left(-\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\right)$$

$$=\frac{N}{q}\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}$$

and $$\frac{C_V}{-k\beta^2}=\left(\frac{\partial U}{\partial\beta}\right)_V=\frac{N}{q}\left(-\sum_J g(J)\varepsilon^2(J)\mathrm{e}^{-\beta\varepsilon(J)}\right)-\frac{N}{q^2}\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\left(\frac{\partial q}{\partial\beta}\right) \quad (1)$$

$$=-\frac{N}{q}\sum_J g(J)\varepsilon^2(J)\mathrm{e}^{-\beta\varepsilon(J)}+\frac{N}{q^2}\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\sum_{J'} g(J')\varepsilon(J')\mathrm{e}^{-\beta\varepsilon(J')}$$

Finally, a double sum appears, one that has some resemblance to the terms in $\zeta(\beta)$. The fact that $\zeta(\beta)$ is a double sum encourages us to try to express the single sum in C_V as a double sum. We can do so by multiplying it by one in the form $\dfrac{\sum_{J'} g(J')\mathrm{e}^{-\beta\varepsilon(J')}}{q}$, so

$$\frac{C_V}{-k\beta^2}=-\frac{N}{q^2}\sum_J g(J)\varepsilon^2(J)\mathrm{e}^{-\beta\varepsilon(J)}\sum_{J'} g(J')\mathrm{e}^{-\beta\varepsilon(J')}+\frac{N}{q^2}\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\sum_{J'} g(J')\varepsilon(J')\mathrm{e}^{-\beta\varepsilon(J')}$$

Now, collect terms within each double sum and divide both sides by $-N$:

$$\frac{C_V}{kN\beta^2}=\frac{1}{q^2}\sum_{J,J'} g(J)g(J')\varepsilon^2(J)\mathrm{e}^{-\beta[\varepsilon(J)+\varepsilon(J')]}-\frac{1}{q^2}\sum_{J,J'} g(J)g(J')\varepsilon(J)\varepsilon(J')\mathrm{e}^{-\beta[\varepsilon(J)+\varepsilon(J')]}$$

Clearly the two sums could be combined, but it pays to make one observation before doing so. The first sum contains a term $\varepsilon^2(J)$, but all the other factors in that sum are related to J and J' in the same way. Thus, the first sum would not be changed by writing $\varepsilon^2(J')$ instead of $\varepsilon^2(J)$; furthermore, if we add the sum with $\varepsilon^2(J')$ to the sum with $\varepsilon^2(J)$, we would have twice the original sum, therefore we can write (finally combining the sums):

$$\frac{C_V}{kN\beta^2}=\frac{1}{2q^2}\sum_{J,J'} g(J)g(J')\mathrm{e}^{-\beta[\varepsilon(J)+\varepsilon(J')]}[\varepsilon^2(J)+\varepsilon^2(J')-2\varepsilon(J)\varepsilon(J')]$$

Recognizing that $\varepsilon^2(J)+\varepsilon^2(J')-2\varepsilon(J)\varepsilon(J')=[\varepsilon(J)-\varepsilon(J')]^2$, we arrive at

$$C_V=\frac{kN\beta^2}{2}\zeta(\beta)$$

For a linear rotor, the degeneracies are $g(J) = 2J + 1$. The energies are

$$\varepsilon(J) = hc\tilde{B}J(J+1) = \theta_R kJ(J+1)$$

so $\beta\varepsilon(J) = \theta_R J(J+1)/T$

The total heat capacity and the contributions of several transitions are plotted in Figure 16.8. One can evaluate $C_{V,m}/R$ using the following expression, derivable from eqn (1) above. It has the advantage of using single sums rather than double sums.

$$\frac{C_{V,\mathrm{m}}}{R} = \frac{1}{q}\sum_J g(J)\beta^2\varepsilon^2(J)\mathrm{e}^{-\beta\varepsilon(J)} - \frac{1}{q^2}\left(\sum_J g(J)\beta\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\right)^2$$

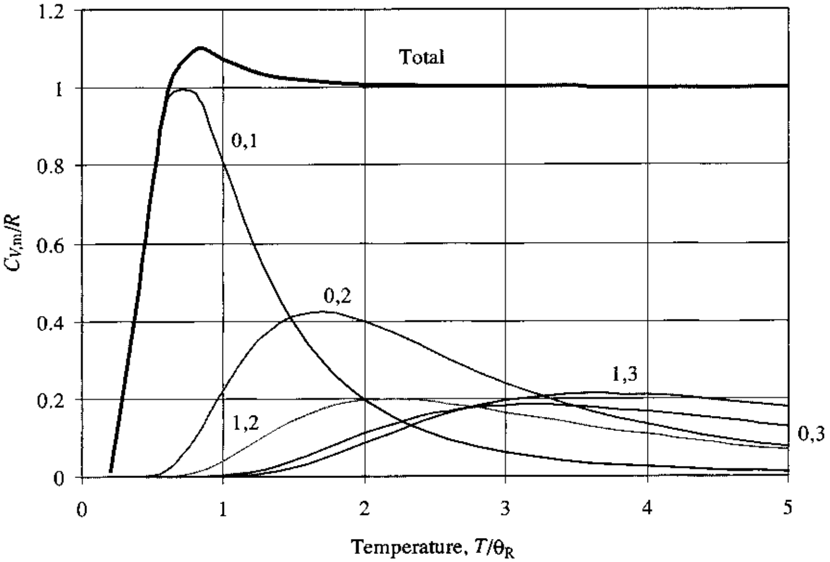


Figure 16.8

COMMENT. $\zeta(\beta)$ is defined in such a way that J and J' each run independently from 0 to infinity. Thus, identical terms appear twice. (For example, both (0,1) and (1,0) terms appear with identical values in $\zeta(\beta)$. In the plot, however, the (0,1) curve represents both terms.) One could redefine the double sum with an inner sum over J' running from 0 to $J - 1$ and an outer sum over J running from 0 to infinity. In that case, each term appears only once, and the overall factor of $\frac{1}{2}$ in C_V would have to be removed.

P16.22 Eqn 16.42 relates the second virial coefficient to the pairwise intermolecular potential energy:

$$B = -2\pi N_A \int_0^\infty fr^2\mathrm{d}r, \quad \text{where} \quad f = \mathrm{e}^{-\beta\varepsilon_P} - 1$$

In order to relate the pairwise potential to the van der Waals equation, we must express that equation as a virial series. The equations are

van der Waals $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$; virial $p = \dfrac{RT}{V_m}\left(1 + \dfrac{B}{V_m} + \cdots\right)$

Expand the van der Waals equation as a power series in $1/V_m$:

$$p=\frac{RT}{V_m(1-b/V_m)}-\frac{a}{V_m^2}=\frac{RT}{V_m}\left(1+\frac{b}{V_m}+\cdots\right)-\frac{a}{V_m^2}\approx\frac{RT}{V_m}\left\{1+\frac{1}{V_m}\left(b-\frac{a}{RT}\right)\right\}$$

Thus, the second virial coefficient in terms of van der Waals parameters is

$$B=b-\frac{a}{RT}$$

The pairwise potential and Mayer *f*-function are:

$$\begin{array}{llll}\text{for } 0\le r<r_1 & E_P\to\infty & e^{-\beta E_P}=0 & f=-1\\ \text{for } r_1\le r<r_2 & E_P\to-\varepsilon & e^{-\beta E_P}=e^{\beta\varepsilon} & f=e^{-\beta\varepsilon}-1>0\\ \text{for } r_2\le r & E_P\to 0 & e^{-\beta E_P}=1 & f=0\end{array}$$

So, $$\frac{B}{-2\pi N_A}=\int_0^\infty fr^2\mathrm{d}r=-\int_0^{r_1}r^2\mathrm{d}r+(e^{\beta\varepsilon}-1)\int_{r_1}^{r_2}r^2\mathrm{d}r=-\frac{r_1^3}{3}+(e^{\beta\varepsilon}-1)\left(\frac{r_2^3}{3}-\frac{r_1^3}{3}\right)$$

Expand the exponential because $\varepsilon\ll kT$, so $\beta\varepsilon\ll1$

$$B\approx-2\pi N_A\left\{-\frac{r_1^3}{3}+(1+\beta\varepsilon-1)\left(\frac{r_2^3}{3}-\frac{r_1^3}{3}\right)\right\}=\frac{2\pi N_A}{3}\left\{r_1^3-\frac{\varepsilon(r_2^3-r_1^3)}{kT}\right\}$$

Comparing this result to the virial coefficient from the van der Waals equation, we identify

$$b=\frac{2\pi N_A r_1^3}{3}\quad\text{and}\quad a=\frac{2\pi N_A\varepsilon_m(r_2^3-r_1^3)}{3}$$

where ε_m is ε expressed as a molar quantity. Thus, the van der Waals b is proportional to the volume of the hard-sphere (repulsive) part of the potential. The a parameter is more complicated, but it is where the attractive part of the potential appears, including both the depth of the attractive well and the range of distances over which it operates.

Use eqn 16.45 to compute the limiting isothermal Joule–Thomson coefficient:

$$\begin{aligned}\lim_{p\to0}\mu_T&=B-T\frac{\mathrm{d}B}{\mathrm{d}T}\\&=\frac{2\pi N_A}{3}\left\{r_1^3-\frac{\varepsilon(r_2^3-r_1^3)}{kT}\right\}-T\frac{2\pi N_A}{3}\left\{\frac{\varepsilon(r_2^3-r_1^3)}{kT^2}\right\}\\&=\frac{2\pi N_A}{3}\left\{r_1^3-\frac{2\varepsilon(r_2^3-r_1^3)}{kT}\right\}=b-\frac{2a}{RT}\end{aligned}$$

The Joule–Thomson coefficient itself is [2.53]

$$\mu=-\frac{\mu_T}{C_p}=\frac{2\pi N_A}{3C_p}\left\{\frac{2\varepsilon(r_2^3-r_1^3)}{kT}-r_1^3\right\}=-\left(\frac{b-\dfrac{2a}{RT}}{C_p}\right)$$

P16.24 All partition functions other than the electronic partition function of atomic I are unaffected by a magnetic field, hence the relative change in K is due to the relative change in q^{E}:

$$q^{\mathrm{E}}=\sum_{M_J}\mathrm{e}^{-g\mu_B\beta\mathcal{B}M_J},\quad M_J=-\tfrac{3}{2},-\tfrac{1}{2},+\tfrac{1}{2},+\tfrac{3}{2};\ g=\tfrac{4}{3}$$

Since $g\mu_{\mathrm{B}}\beta\mathcal{B}\ll 1$ for normally attainable fields, we can expand the exponentials

$$q^{\mathrm{E}}=\sum_{M_J}\left\{1-g\mu_B\beta\mathcal{B}M_J+\frac{1}{2}(g\mu_B\beta\mathcal{B}M_J)^2+\cdots\right\}$$

$$\approx 4+\frac{1}{2}(g\mu_B\beta\mathcal{B})^2\sum_{M_J}M_J^2\left[\sum_{M_J}M_J=0\right]$$

$$=4\left(1+\frac{10}{9}(\mu_B\beta\mathcal{B})^2\right)\quad\left[g=\frac{4}{3}\right]$$

This partition function appears squared in the numerator of the equilibrium constant expression. (See solution to Exercise 16.20(a).) Therefore, if K is the actual equilibrium constant and K^0 is its value when $\mathcal{B}=0$, we write

$$\frac{K}{K^0}=\left(1+\frac{10}{9}(\mu_B\beta\mathcal{B})^2\right)^2\approx 1+\frac{20}{9}\mu_{\mathrm{B}}^2\beta^2\mathcal{B}^2$$

For a shift of 1%, we require

$$\tfrac{20}{9}\mu_{\mathrm{B}}^2\beta^2\mathcal{B}^2\approx 0.01,\quad\text{or}\quad \mu_{\mathrm{B}}\beta\mathcal{B}\approx 0.067$$

Hence,

$$\mathcal{B}\approx\frac{0.067kT}{\mu_B}=\frac{(0.067)\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(1000\,\mathrm{K})}{9.274\times10^{-24}\,\mathrm{J\,T^{-1}}}\approx\boxed{100\,\mathrm{T}}$$

Solutions to applications

P16.26 $S=k\ln W$[15.27]

so $S=k\ln 4^N=Nk\ln 4$

$$=(5\times10^8)\times(1.38\times10^{-23}\,\mathrm{J\,K^{-1}})\times\ln 4$$

$$=\boxed{9.57\times10^{-15}\,\mathrm{J\,K^{-1}}}$$

Question. Is this a large residual entropy? The answer depends on what comparison is made. Multiply the answer by Avogadro's number to obtain the molar residual entropy, 5.76×10^9 J K^{-1} mol^{-1}, surely a large number—but then DNA is a macromolecule. The residual entropy per mole of base pairs may be a more reasonable quantity to compare to molar residual entropies of small molecules. To obtain that answer, divide the molecule's entropy by the number of base pairs before multiplying by N_{A}. The result is 11.5 J K^{-1} mol^{-1}, a quantity more in line with examples discussed in Section 16.7.

P16.28 The standard molar Gibbs energy is given by

$$G_m^\ominus - G_m^\ominus(0) = RT\ln\frac{q_m^\ominus}{N_A}, \quad \text{where} \quad \frac{q_m^\ominus}{N_A} = \frac{q_m^{T\ominus}}{N_A}q^R q^V q^E \ [16.51]$$

Translation: (See the solution to Problem 16.6 for all partition functions.)

$$\frac{q_m^{T\ominus}}{N_A} = 2.561\times10^{-2}(T/\mathrm{K})^{5/2}(M/\mathrm{g\ mol^{-1}})^{3/2}$$
$$= (2.561\times10^{-2})\times(2000)^{5/2}\times(38.90)^{3/2} = 1.111\times10^{9}$$

Rotation of a linear molecule:

$$q^R = \frac{kT}{\sigma hc\tilde{B}} = \frac{0.6950}{\sigma}\times\frac{T/\mathrm{K}}{\tilde{B}/\mathrm{cm^{-1}}}$$

The rotational constant is

$$\tilde{B} = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c m_{\mathrm{eff}}R^2}$$

where $m_{\mathrm{eff}} = \dfrac{m_B m_{Si}}{m_B + m_{Si}} = \dfrac{(10.81)\times(28.09)}{10.81+28.09}\times\dfrac{10^{-3}\ \mathrm{kg\ mol^{-1}}}{6.022\times10^{23}\ \mathrm{mol^{-1}}} = 1.296\times10^{-26}\ \mathrm{kg}$

$$\tilde{B} = \frac{1.0546\times10^{-34}\ \mathrm{J\ s}}{4\pi(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times(1.296\times10^{-26}\ \mathrm{kg})\times(190.5\times10^{-12}\ \mathrm{m})^2} = 0.5952\ \mathrm{cm^{-1}}$$

so $q^R = \dfrac{0.6950}{1}\times\dfrac{2000}{0.5952} = 2335$

Vibration:

$$q^V = \frac{1}{1-e^{-hc\tilde{\nu}/kT}} = \frac{1}{1-\exp\left(\dfrac{-1.4388(\tilde{\nu}/\mathrm{cm^{-1}})}{T/\mathrm{K}}\right)} = \frac{1}{1-\exp\left(\dfrac{-1.4388(772)}{2000}\right)} = 2.467$$

The Boltzmann factor for the lowest-lying electronic excited state is

$$\exp\left(\frac{-(1.4388)\times(8000)}{2000}\right) = 3.2\times10^{-3}$$

The degeneracy of the ground level is 4 (spin degeneracy = 4, orbital degeneracy = 1), and that of the excited level is also 4 (spin degeneracy = 2, orbital degeneracy = 2), so

$$q^E = 4(1+3.2\times10^{-3}) = 4.013$$

Putting it all together yields

$$G_m^\ominus - G_m^\ominus(0) = (8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(2000\ \mathrm{K})$$
$$\times\ln[(1.111\times10^{9})\times(2335)\times(2.467)\times(4.013)]$$
$$= 5.135\times10^{5}\ \mathrm{J\ mol^{-1}} = \boxed{513.5\ \mathrm{kJ\ mol^{-1}}}$$

P16.30 The standard molar Gibbs energy is given by

$$G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) = RT\ln\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}}, \quad \text{where} \quad \frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}} = \frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}} q^{\mathrm{R}} q^{\mathrm{V}} q^{\mathrm{E}} \ [16.51]$$

See Problem 16.28 above for partition function expressions. First, at 10.00 K

$$\text{Translation:} \quad \frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}} = 2.561 \times 10^{-2}(T/\mathrm{K})^{5/2}(M/\mathrm{g\ mol^{-1}})^{3/2}$$
$$= (2.561 \times 10^{-2}) \times (10.00)^{5/2} \times (36.033)^{3/2} = 1752$$

Rotation of a non-linear molecule:

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} = \frac{1.0270}{\sigma} \times \frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm^{-3}})^{1/2}}$$

The rotational constants are

$$\tilde{B} = \frac{\hbar}{4\pi c I}, \quad \text{so} \quad \tilde{A}\tilde{B}\tilde{C} = \left(\frac{\hbar}{4\pi c}\right)^3 \frac{1}{I_{\mathrm{A}} I_{\mathrm{B}} I_{\mathrm{C}}},$$

$$\tilde{A}\tilde{B}\tilde{C} = \left(\frac{1.0546 \times 10^{-34}\ \mathrm{J\ s}}{4\pi(2.998 \times 10^{10}\ \mathrm{cm\ s^{-1}})}\right)^3$$
$$\times \frac{(10^{10}\ \text{Å}\ \mathrm{m^{-1}})^6}{(39.340) \times (39.032) \times (0.3082) \times (m_{\mathrm{u}}\ \text{Å}^2)^3 \times (1.66054 \times 10^{-27}\ \mathrm{kg\ u^{-1}})^3}$$
$$= 101.2\ \mathrm{cm^{-3}}$$

$$\text{so} \quad q^{\mathrm{R}} = \frac{1.0270}{2} \times \frac{(10.00)^{3/2}}{(101.2)^{1/2}} = 1.614$$

Vibration: for each mode

$$q^{\mathrm{V}} = \frac{1}{1 - \mathrm{e}^{-hc\tilde{\nu}/kT}} = \frac{1}{1 - \exp\left(\dfrac{-1.4388(\tilde{\nu}/\mathrm{cm^{-1}})}{T/\mathrm{K}}\right)} = \frac{1}{1 - \exp\left(\dfrac{-1.4388(63.4)}{10.00}\right)} = 1.0001$$

Even the lowest-frequency mode has a vibrational partition function of 1, so the stiffer vibrations have q^{V} even closer to 1. The degeneracy of the electronic ground state is 1, so $q^{\mathrm{E}} = 1$. Putting it all together yields

$$G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) = (8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}) \times (10.00\ \mathrm{K})\ln[(1752) \times (1.614) \times (1) \times (1)]$$
$$= \boxed{660.8\ \mathrm{J\ mol^{-1}}}$$

Now, at 1000 K

$$\text{Translation:} \quad \frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}} = (2.561 \times 10^{-2}) \times (1000)^{5/2} \times (36.033)^{3/2} = 1.752 \times 10^8$$

$$\text{Rotation:} \quad q^{\mathrm{R}} = \frac{1.0270}{2} \times \frac{(1000)^{3/2}}{(101.2)^{1/2}} = 1614$$

Vibration: $q_1^{\mathrm{V}} = \dfrac{1}{1-\exp(-\frac{(1.4388)\times(63.4)}{1000})} = 11.47$

$$q_2^{\mathrm{V}} = \frac{1}{1-\exp(-\frac{(1.4388)\times(1224.5)}{1000})} = 1.207$$

$$q_3^{\mathrm{V}} = \frac{1}{1-\exp(-\frac{(1.4388)\times(2040)}{1000})} = 1.056$$

$$q^{\mathrm{V}} = (11.47)\times(1.207)\times(1.056) = 14.62$$

Putting it all together yields

$$\begin{aligned} G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) &= (8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(1000\ \mathrm{K})\times\ln[(1.752\times10^{8})\times(1614)\times(14.62)\times(1)] \\ &= 2.415\times10^{5}\ \mathrm{J\ mol^{-1}} = \boxed{241.5\ \mathrm{kJ\ mol^{-1}}} \end{aligned}$$

17 Molecular interactions

Answers to discussion questions

D17.2 When the applied field changes direction slowly, the permanent dipole moment has time to reorientate—the whole molecule rotates into a new direction—and follows the field. However, when the frequency of the field is high, a molecule cannot change direction fast enough to follow the change in direction of the applied field and the dipole moment then makes no contribution to the polarization of the sample. Because a molecule takes about 1 ps to turn through about 1 radian in a fluid, the loss of this contribution to the polarization occurs when measurements are made at frequencies greater than about 10^{11} Hz (in the microwave region). We say that the **orientation polarization**, the polarization arising from the permanent dipole moments, is lost at such high frequencies.

The next contribution to the polarization to be lost as the frequency is raised is the **distortion polarization**, the polarization that arises from the distortion of the positions of the nuclei by the applied field. The molecule is bent and stretched by the applied field, and the molecular dipole moment changes accordingly. The time taken for a molecule to bend is approximately the inverse of the molecular vibrational frequency, so the distortion polarization disappears when the frequency of the radiation is increased through the infrared. The disappearance of polarization occurs in stages: as shown in *Justification* 17.3, each successive stage occurs as the incident frequency rises above the frequency of a particular mode of vibration.

At even higher frequencies, in the visible region, only the electrons are mobile enough to respond to the rapidly changing direction of the applied field. The polarization that remains is now due entirely to the distortion of the electron distribution, and the surviving contribution to the molecular polarizability is called the **electronic polarizability**.

D17.4 (a) $V = -\dfrac{Q_2\mu_1}{4\pi\varepsilon_0 r^2}$ [17.18]

V is the potential energy of interaction between a point dipole μ_1 and the point charge Q_2 at the separation r. The point charge lies on the axis of the dipole and the separation r is much larger than the separation of charge within the dipole so that the partial charges of the dipole seem to merge and cancel to create the so-called **point dipole**.

(b) $V = -\dfrac{Q_2\mu_1\cos\theta}{4\pi\varepsilon_0 r^2}$

V is the potential energy of interaction between a point dipole μ_1 and the point charge Q_2 at the separation r. The point charge lies at an angle θ to the axis of the dipole and the separation r is much larger than the separation of charge within the dipole so that the partial charges of the dipole seem to merge and cancel.

(c) $V = \dfrac{\mu_1\mu_2 f(\theta)}{4\pi\varepsilon_0 r^3}$, where $f(\theta) = 1 - 3\cos^2\theta$ [17.22]

V is the potential energy of interaction between the two point dipoles μ_1 and μ_2 at the separation r. The dipoles are parallel and the separation distance is at angle θ to the dipoles. The separation r is much larger than the separation of charge within the dipoles so that the partial charges of the dipoles seem to merge and cancel.

D17.6 There are three van der Waals type interactions that depend on distance as $1/r^6$; they are the Keesom interaction between rotating permanent dipoles, the permanent-dipole–induced-dipole interaction, and the induced-dipole–induced-dipole, or London dispersion, interaction. In each case, we can visualize the distance dependence of the potential energy as arising from the $1/r^3$ dependence of the field (and hence the magnitude of the induced dipole) and the $1/r^3$ dependence of the potential energy of interaction of the dipoles (either permanent or induced).

D17.8 The increase in entropy of a solution when hydrophobic molecules or groups of molecules cluster together and reduce their structural demands on the solvent (water) is the origin of the hydrophobic interaction that tends to stabilize clustering of hydrophobic groups in solution. A manifestation of the hydrophobic interaction is the clustering together of hydrophobic groups in biological macromolecules. For example, the side chains of amino acids that are used to form the polypeptide chains of proteins are hydrophobic, and the hydrophobic interaction is a major contributor to the tertiary structure of polypeptides. At first thought, this clustering would seem to be a non-spontaneous process as the clustering of the solute results in a decrease in entropy of the solute. However, the clustering of the solute results in greater freedom of movement of the solvent molecules and an accompanying increase in disorder and entropy of the solvent. The total entropy of the system has increased and the process is spontaneous.

D17.10 A molecular beam is a narrow stream of molecules with a narrow spread of velocities and, in some cases, in specific internal states or orientations. Molecular beam studies of non-reactive collisions are used to explore the details of intermolecular interactions with a view to determining the shape of the intermolecular potential.

The primary experimental information from a molecular beam experiment is the fraction of the molecules in the incident beam that are scattered into a particular direction. The fraction is normally expressed in terms of dI, the rate at which molecules are scattered into a cone that represents the area covered by the 'eye' of the detector (Figure 17.15 of the text). This rate is reported as the differential scattering cross-section, σ, the constant of proportionality between the value of dI and the intensity I of the incident beam, the number density of target molecules, $\mathcal{N}$, and the infinitesimal path length dx through the sample:

$\mathrm{d}I = \sigma I \mathcal{N} \mathrm{d}x$ [17.35]

The value of σ (which has the dimensions of area) depends on the impact parameter, b, the initial perpendicular separation of the paths of the colliding molecules (text Figure 17.16), and the details of the intermolecular potential.

The scattering pattern of real molecules, which are not hard spheres, depends on the details of the intermolecular potential, including the anisotropy that is present when the molecules are non-spherical. The scattering also depends on the relative speed of approach of the two particles: a very fast particle might pass through the interaction region without much deflection, whereas a slower one on the same path might be temporarily captured and undergo considerable deflection (text Figure 17.18). The variation of the scattering cross-section with the relative speed of approach therefore gives information about the strength and range of the intermolecular potential.

Another phenomenon that can occur in certain beams is the capturing of one species by another. The vibrational temperature in supersonic beams is so low that van der Waals molecules may be formed, which are complexes of the form AB in which A and B are held together by van der Waals forces or hydrogen bonds. Large numbers of such molecules have been studied spectroscopically, including ArHCl, $(HCl)_2$, $ArCO_2$, and $(H_2O)_2$. More recently, van der Waals clusters of water molecules have been pursued as far as $(H_2O)_6$. The study of their spectroscopic properties gives detailed information about the intermolecular potentials involved.

Solutions to exercises

E17.1(b) A molecule that has a centre of symmetry cannot be polar. SO_3, which has a trigonal planar structure (D_{3h}), and XeF_4, which is square planar (D_{4h}), cannot be polar. $\boxed{SF_4}$ (see-saw, C_{2v}) may be polar.

E17.2(b)

$$\begin{aligned}\mu_{\text{res}} &= (\mu_1^2+\mu_2^2+2\mu_1\mu_2\cos\theta)^{1/2}\ [17.2\text{a}]\\ &= [(2.5)^2+(0.50)^2+(2)\times(2.5)\times(0.50)\times(\cos 120°)]^{1/2}\,\text{D} = \boxed{2.3\ \text{D}}\end{aligned}$$

E17.3(b)

$$\mu = \sum_i Q_i\boldsymbol{r}_i = 4e(0) - 2e\boldsymbol{r}_2 - 2e\boldsymbol{r}_3, \quad \text{where} \quad \boldsymbol{r}_2 = \mathbf{i}x_2 \quad \text{and} \quad \boldsymbol{r}_3 = \mathbf{i}x_3 + \mathbf{j}y_3$$

$$x_2 = +162\ \text{pm}$$

$$x_3 = r_3\cos 30° = (+143\ \text{pm})\times(0.86\bar{6}) = 12\bar{4}\ \text{pm}$$

$$y_3 = r_3\sin 30° = (143\ \text{pm})\times(0.50\bar{0}) = 71.5\ \text{pm}$$

The components of the vector sum are the sums of the components.

$$\mu_x = -2ex_2 - 2ex_3 = -2e\times\{(162)+(12\bar{4})\}\ \text{pm} = -e\times(57\bar{2}\ \text{nm})$$

$$\mu_y = -2ey_3 = -2e\times(71.5\ \text{pm}) = -e\times(143\ \text{pm})$$

$$\begin{aligned}\mu &= (\mu_x^2+\mu_y^2)^{1/2}\ [17.3\text{b}]\\ &= e\times\{(57\bar{2}\ \text{pm})^2+(143\ \text{pm})^2\}^{1/2} = (1.602\times10^{-19}\ \text{C})\times(59\bar{0}\times10^{-12}\ \text{m})\\ &= (9.4\bar{5}\times10^{-29}\ \text{C m})\times\left(\frac{1\ \text{D}}{3.33564\times10^{-30}\ \text{C m}}\right) = \boxed{28\ \text{D}}\end{aligned}$$

The angle that μ makes with the x-axis is given by

$$\cos\theta = \frac{|\mu_x|}{\mu} = \frac{57\bar{2}}{59\bar{0}}, \quad \text{so} \quad \theta = \cos^{-1}\left(\frac{57\bar{2}}{59\bar{0}}\right) = \boxed{14.\bar{2}°}$$

E17.4(b) The H–Cl bond length of a hydrogen chloride molecule is 127.45 pm and the Mg^{2+} cation is 300 pm from the dipole centre. Because these lengths are comparable, a calculation based on the assumption that the hydrogen chloride dipole acts like a point dipole with a dipole length much shorter than the dipole–ion distance is unlikely to provide an accurate value of the dipole–ion interaction energy. However, such a calculation does provide an 'order-of-magnitude' estimate. The minimum value of the dipole–ion interaction occurs with the dipole pointing toward the cation.

$$V_{\min} \sim -\frac{\mu_{\mathrm{HCl}} Q_{\mathrm{Mg}^{2+}}}{4\pi\varepsilon_0 r^2}\,[17.18] = -\frac{2\mu_{\mathrm{HCl}} e}{4\pi\varepsilon_0 r^2}$$

$$\sim -\frac{2\times(1.08\ \mathrm{D})\times(3.336\times10^{-30}\ \mathrm{C\ m\ D^{-1}})\times(1.602\times10^{-19}\ \mathrm{C})}{(1.113\times10^{-10}\ \mathrm{J^{-1}\ C^2\ m^{-1}})\times(300\times10^{-12}\ \mathrm{m})^2}$$

$$\sim -1.15\times10^{-19}\ \mathrm{J}$$

The interaction potential becomes a maximum on flipping the dipole. This effectively changes the sign of the dipole in the previous calculation, giving

$$V_{\max} \sim 1.15\times10^{-19}\ \mathrm{J}$$

The work w required to flip the dipole is the difference $V_{\max} - V_{\min}$:

$$w \sim V_{\max} - V_{\min} = 2.30\times10^{-18}\ \mathrm{J}$$

$$w_{\mathrm{m}} = wN_{\mathrm{A}} \sim \boxed{1.39\times10^{3}\ \mathrm{kJ\ mol^{-1}}}$$

E17.5(b) The induced dipole moment of NH_3 is

$$\begin{aligned}\mu^*_{\mathrm{NH_3}} &= \alpha\mathcal{E}\,[17.4] = 4\pi\varepsilon_0\alpha'_{\mathrm{NH_3}}\mathcal{E}\,[17.5]\\ &= 4\pi\times(8.854\times10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}})\times(2.22\times10^{-30}\ \mathrm{m^3})\times(15.0\times10^{3}\ \mathrm{V\ m^{-1}})\,[1\ \mathrm{J} = 1\ \mathrm{C\ V}]\\ &= (3.71\times10^{-36}\ \mathrm{C\ m})\times\left(\frac{1\ \mathrm{D}}{3.33564\times10^{-30}\ \mathrm{C\ m}}\right)\\ &= \boxed{1.00\ \mu\mathrm{D}}\end{aligned}$$

Thus, we see that the induced dipole is much smaller than the permanent dipole moment of NH_3 (1.47 D).

E17.6(b) Polarizability α, dipole moment μ, and molar polarization P_{m} are related by

$$P_{\mathrm{m}} = \left(\frac{N_{\mathrm{A}}}{3\varepsilon_0}\right)\times\left(\alpha + \frac{\mu^2}{3kT}\right)[17.15]$$

In order to solve for α, it is first necessary to obtain μ from the temperature variation of P_{m}:

$$\alpha + \frac{\mu^2}{3kT} = \frac{3\varepsilon_0 P_{\mathrm{m}}}{N_{\mathrm{A}}}$$

Therefore, $\left(\frac{\mu^2}{3k}\right)\times\left(\frac{1}{T} - \frac{1}{T'}\right) = \left(\frac{3\varepsilon_0}{N_{\mathrm{A}}}\right)\times(P_{\mathrm{m}} - P'_{\mathrm{m}})$ [P_{m} at T, P'_{m} at T']

and hence,

$$\mu^2 = \frac{9\varepsilon_0 k \times (P_\mathrm{m} - P'_\mathrm{m})}{N_\mathrm{A} \times \left(\dfrac{1}{T} - \dfrac{1}{T'}\right)}$$

$$= \frac{9 \times (8.854 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}}) \times (1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (75.74 - 71.43) \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}}{(6.022 \times 10^{23}\ \mathrm{mol^{-1}}) \times \left(\dfrac{1}{320.0\ \mathrm{K}} - \dfrac{1}{421.7\ \mathrm{K}}\right)}$$

$$= 1.04\bar{5} \times 10^{-59}\ \mathrm{C^2\,m^2}$$

$$\mu = 3.23 \times 10^{-30}\ \mathrm{C\,m} \times \left(\frac{1\ \mathrm{D}}{3.33564 \times 10^{-30}\ \mathrm{C\,m}}\right) = \boxed{0.968\ \mathrm{D}}$$

$$\alpha = \frac{3\varepsilon_0 P_\mathrm{m}}{N_\mathrm{A}} - \frac{\mu^2}{3kT} = \frac{3 \times (8.854 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}}) \times (75.74 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}})}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}}$$

$$- \frac{1.04\bar{5} \times 10^{-59}\ \mathrm{C^2\,m^2}}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (320.0\ \mathrm{K})}$$

$$= \boxed{2.56 \times 10^{-39}\ \mathrm{J^{-1}\,C^2\,m^2}}$$

Corresponding to $\alpha' = \dfrac{\alpha}{4\pi\varepsilon_0}$ [17.5] $= \boxed{2.29 \times 10^{-29}\ \mathrm{m^3}}$

E17.7(b) $M = 85.0\ \mathrm{g\,mol^{-1}}$

$$\varepsilon_\mathrm{r} - 1 = \frac{\rho P_\mathrm{m}}{M} \times (\varepsilon_\mathrm{r} + 2)\ [17.14]$$

$$\left(1 - \frac{\rho P_\mathrm{m}}{M}\right)\varepsilon_\mathrm{r} = 1 + \frac{2\rho P_\mathrm{m}}{M}$$

$$\varepsilon_\mathrm{r} = \frac{M + 2\rho P_\mathrm{m}}{M - \rho P_\mathrm{m}} = \frac{85.0\ \mathrm{g\,mol^{-1}} + 2 \times (1.92\ \mathrm{g\,cm^{-3}}) \times (32.16\ \mathrm{cm^3\,mol^{-1}})}{85.0\ \mathrm{g\,mol^{-1}} - (1.92\ \mathrm{g\,cm^{-3}}) \times (32.16\ \mathrm{cm^3\,mol^{-1}})} = \boxed{8.97}$$

E17.8(b) $n_\mathrm{r} = (\varepsilon_\mathrm{r})^{1/2}$ [17.17] and $\dfrac{\varepsilon_\mathrm{r} - 1}{\varepsilon_\mathrm{r} + 2} = \dfrac{\rho N_\mathrm{A} \alpha}{3M\varepsilon_0}$ [17.16]

Therefore,

$$\alpha = \frac{3M\varepsilon_0}{\rho N_\mathrm{A}}\left(\frac{n_\mathrm{r}^2 - 1}{n_\mathrm{r}^2 + 2}\right) = \frac{3 \times (65.5\ \mathrm{g\,mol^{-1}}) \times (8.854 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}})}{(2.99 \times 10^{6}\ \mathrm{g\,m^{-3}}) \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})} \times \left(\frac{1.622^2 - 1}{1.622^2 + 2}\right)$$

$$= \boxed{3.40 \times 10^{-40}\ \mathrm{J^{-1}\,C^2\,m^2}}$$

E17.9(b) $\alpha' = \dfrac{\alpha}{4\pi\varepsilon_0}$ [17.5]

$$\alpha = 4\pi\varepsilon_0\alpha' = (1.11265 \times 10^{-10}\ \mathrm{J^{-1}\,C^2\,m^{-1}}) \times (2.2 \times 10^{-30}\ \mathrm{m^3}) = 2.4\bar{5} \times 10^{-40}\ \mathrm{J^{-1}\,C^2\,m^2}$$

Let

$$C=\frac{\rho N_{\mathrm{A}}\alpha}{3M\varepsilon_0}=\frac{(865\times10^{3}\,\mathrm{g\,m^{-3}})\times(6.022\times10^{23}\,\mathrm{mol^{-1}})\times(2.4\bar{5}\times10^{-40}\,\mathrm{J^{-1}\,C^{2}\,m^{2}})}{3\times(72.3\,\mathrm{g\,mol^{-1}})\times(8.85419\times10^{-12}\,\mathrm{J^{-1}\,C^{2}\,m^{-1}})}=0.066\bar{5}$$

and solve the Clausius–Mossotti eqn [17.16] for ε_{r} with which we calculate the refractive index.

$$\frac{\varepsilon_{\mathrm{r}}-1}{\varepsilon_{\mathrm{r}}+2}=C\ [17.16,\text{ the Clausius–Mossotti eqn}]$$

$$\varepsilon_{\mathrm{r}}=\frac{1+2C}{1-C}=\frac{1+2\times(0.066\bar{5})}{1-0.066\bar{5}}=1.2137$$

$$n_{\mathrm{r}}=\varepsilon_{\mathrm{r}}^{1/2}\ [17.17]=(1.2137)^{1/2}=\boxed{1.10}$$

E17.10(b) $\mu=5.17\times10^{-30}\,\mathrm{C\,m}$ for bromobenzene ($157.00\,\mathrm{g\,mol^{-1}}$)

$$\alpha=4\pi\varepsilon_0\alpha'\,[17.5]=(1.11265\times10^{-10}\,\mathrm{J^{-1}\,C^{2}\,m^{-1}})\times(1.5\times10^{-29}\,\mathrm{m^{3}})=1.6\bar{7}\times10^{-39}\,\mathrm{J^{-1}\,C^{2}\,m^{2}}$$

$$P_{\mathrm{m}}=\frac{N_{\mathrm{A}}}{3\varepsilon_0}\left(\alpha+\frac{\mu^2}{3kT}\right)[17.15]=\frac{6.022\times10^{23}\,\mathrm{mol^{-1}}}{3\times(8.85419\times10^{-12}\,\mathrm{J^{-1}\,C^{2}\,m^{-1}})}$$

$$\times\left((1.6\bar{7}\times10^{-39}\,\mathrm{J^{-1}\,C^{2}\,m^{2}})+\frac{(5.17\times10^{-30}\,\mathrm{C\,m})^2}{3\times(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298.15\,\mathrm{K})}\right)$$

$$=8.6\bar{9}\times10^{-5}\,\mathrm{m^{3}\,mol^{-1}}$$

Let

$$C=\frac{\rho P_{\mathrm{m}}}{M}=\frac{(1.491\times10^{6}\,\mathrm{g\,m^{-3}})\times(8.6\bar{9}\times10^{-5}\,\mathrm{m^{3}\,mol^{-1}})}{157.00\,\mathrm{g\,mol^{-1}}}=0.82\bar{5}$$

and solve the Debye eqn [17.14] for ε_{r}.

$$\frac{\varepsilon_{\mathrm{r}}-1}{\varepsilon_{\mathrm{r}}+2}=C\ [17.14,\text{ the Debye eqn}]$$

$$\varepsilon_{\mathrm{r}}=\frac{1+2C}{1-C}=\frac{1+2\times(0.82\bar{5})}{1-0.82\bar{5}}=\boxed{15}$$

E17.11(b)

$$V_{\mathrm{London}}=-\frac{3(\alpha'_{\mathrm{Ar}}I_{\mathrm{Ar}})^2}{2(I_{\mathrm{Ar}}+I_{\mathrm{Ar}})r^6}\,[17.25]=-\frac{3(\alpha'_{\mathrm{Ar}})^2I_{\mathrm{Ar}}}{4r^6}$$

$$=-\frac{3\times(1.66\times10^{-30}\,\mathrm{m^{3}})^2\times(1520.4\,\mathrm{kJ\,mol^{-1}})}{4\times(1.0\times10^{-9}\,\mathrm{m})^6}$$

$$=\boxed{3.1\,\mathrm{J\,mol^{-1}}}$$

E17.12(b) Using the partial charge presented in Table 17.2, we estimate the partial charge on each hydrogen atom of a water molecule to be $Q_{\mathrm{H}}=\delta e$ where $\delta=0.42$. The electroneutrality of an H_2O molecule implies that the estimated partial charge on the oxygen atom is $Q_{\mathrm{O}}=-2\delta e$. With a hydrogen bond length of 170 pm, the point charge model of the hydrogen bond in a continuum of water estimates the potential of interaction to be

$$V = \frac{Q_H Q_O}{4\pi\varepsilon r} = -\frac{2(\delta e)^2}{4\pi\varepsilon_r\varepsilon_0 r}\,[17.12\text{b}]$$

$$= -\frac{2(0.42 \times 1.60 \times 10^{-19}\,\text{C})^2}{4\pi(80) \times (8.85 \times 10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1}) \times (170 \times 10^{-12}\,\text{m})} = -6.0 \times 10^{-21}\,\text{J}$$

The molar energy required to break these bonds is

$$E_m = -N_A V = -(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (-6.0 \times 10^{-21}\,\text{J}) = \boxed{3.6\,\text{kJ mol}^{-1}}$$

The model of point charges embedded within a continuum of water yields an estimate of the hydrogen bond strength that is well below the experimental value of about 20 kJ mol^{-1}. The excessively low estimate has been caused by the assumption that water around the point charges behaves as a continuum of matter. This significantly overestimates the ability of the surrounding water molecules to modulate the point-charge interaction.

E17.13(b)

$$V_m = \frac{M}{\rho} = \frac{18.02\,\text{g mol}^{-1}}{0.9940\,\text{g cm}^{-3}} = 18.13\,\text{cm}^3$$

$$p = p^* e^{2\gamma V_m(1)/rRT}\,[17.51,\text{ the Kelvin eqn}]$$

$$= (5.623\,\text{kPa}) \times \exp\left\{\frac{2 \times (72.75 \times 10^{-3}\,\text{N m}^{-1}) \times (18.13 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})}{(20.0 \times 10^{-9}\,\text{m}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (308.15\,\text{K})}\right\}$$

$$= \boxed{5.92\,\text{kPa}}$$

E17.14(b)

$$\gamma = \tfrac{1}{2}\rho g r h\,[17.40]$$
$$= \tfrac{1}{2} \times (995.6\,\text{kg m}^{-3}) \times (9.80665\,\text{m s}^{-2}) \times (0.320 \times 10^{-3}\,\text{m}) \times (9.11 \times 10^{-2}\,\text{m})$$
$$= 0.142\bar{3}\,\text{kg s}^{-2} = \boxed{142\,\text{mN m}^{-1}}$$

E17.15(b)

$$p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{r}\,[17.38,\text{ the Laplace eqn}] = \frac{2 \times (22.39 \times 10^{-3}\,\text{N m}^{-1})}{220 \times 10^{-9}\,\text{m}}$$

$$= 2.04 \times 10^5\,\text{N m}^{-2} = \boxed{204\,\text{kPa}}$$

Pressure differentials for small droplets are quite large.

Solutions to problems

Solutions to numerical problems

P17.2 Refer to Figure 17.1 of the text, and add moments vectorially using $\mu = 2\mu_1 \cos\tfrac{1}{2}\theta$ [17.2b].

(a) *p*-xylene: the resultant is zero, so $\mu = \boxed{0}$

(b) *o*-xylene: $\mu = (2) \times (0.4\,\text{D}) \times \cos 30° = \boxed{0.7\,\text{D}}$

(c) *m*-xylene $\mu = (2) \times (0.4\,\text{D}) \times \cos 60° = \boxed{0.4\,\text{D}}$

The *p*-xylene molecule belongs to the group D_{2h}, and so it is necessarily non-polar.

P17.4 The energy of the dipole is $-\mu_1\mathcal{E}$ in the electric field $\mathcal{E}$. To flip it over requires a change in energy of $2\mu_1\mathcal{E}$. This will occur when the energy of interaction of the dipole with the induced dipole of the Ar atom equals $2\mu_1\mathcal{E}$. The magnitude of the dipole–induced-dipole interaction is

$$|V| = \frac{\mu_1^2\alpha_2'}{4\pi\varepsilon_0 r^6}\ [17.24] = 2\mu_1\mathcal{E}\ [\text{after flipping over}]$$

$$r^6 = \frac{\mu_1\alpha_2'}{8\pi\varepsilon_0\mathcal{E}} = \frac{(6.17\times10^{-30}\ \text{C m})\times(1.66\times10^{-30}\ \text{m}^3)}{(8\pi)\times(8.854\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})\times(1.0\times10^{3}\ \text{V m}^{-1})} = 4.6\times10^{-53}\ \text{m}^6$$

$$r = 1.9\times10^{-9}\ \text{m} = \boxed{1.9\ \text{nm}}$$

COMMENT. This distance is about 11 times the radius of the Ar atom.

P17.6

$$P_\text{m} = \frac{M}{\rho}\times\left(\frac{\varepsilon_\text{r}-1}{\varepsilon_\text{r}+2}\right)[17.14]\ \text{and}\ P_\text{m} = \frac{4\pi}{3}N_\text{A}\alpha' + \frac{N_\text{A}\mu^2}{9\varepsilon_0 kT}\ [17.15,\ \text{with}\ \alpha = 4\pi\varepsilon_0\alpha']$$

Eqn 17.15 indicates that, when the permanent dipole moment μ contributes to the molar polarization in a manner that is consistent with thermal averaging of the electric dipole moment in the presence of the applied field (i.e. free rotation), a plot of P_m against $1/T$ should be linear with an intercept at $1/T = 0$ equal to $\frac{4\pi}{3}N_\text{A}\alpha'$ and a constant slope for which $\frac{\text{d}P_\text{m}}{\text{d}(1/T)}$ equals $\frac{N_\text{A}\mu^2}{9\varepsilon_0 k}$. Eqn 17.15 is replaced by the Clausius–Mossotti expression, $P_\text{m} = \frac{4\pi}{3}N_\text{A}\alpha'$ [17.16], in the case for which either the molecules are non-polar or because the frequency of the applied field is so high that the molecules cannot orientate quickly enough to follow the change in direction of the field.

To examine the possibility that either solid or liquid methanol exhibits the characteristics of eqn 17.14 or eqn 17.16, we draw up the following table and prepare the Figure 17.1 plot of P_m against $1/T$. The molar polarization P_m is calculated with eqn 17.14 at all temperatures and, since the data have been corrected for the variation in methanol density, we use $\rho = 0.791\ \text{g cm}^{-3}$ for all entries and $M = 32.0\ \text{g mol}^{-1}$.

$\theta/°\text{C}$	−185	−170	−150	−140	−110	−80	−50	−20	0	20
T/K	88	103	123	133	163	193	223	253	273	293
$\frac{1000}{T/\text{K}}$	11.3	9.69	8.12	7.51	6.13	5.18	4.48	3.95	3.66	3.41
ε_r	3.2	3.6	4	5.1	67	57	49	43	38	34
$\frac{\varepsilon_\text{r}-1}{\varepsilon_\text{r}+2}$	0.42	0.46	0.50	0.58	0.957	0.949	0.941	0.933	0.925	0.917
$P_\text{m}/(\text{cm}^3\ \text{mol}^{-1})$	17.1	18.8	20.2	23.4	38.7	38.4	38.1	37.7	37.4	37.1

Inspection of Figure 17.1 reveals that the molar polarization P_m is not a linear function of $1/T$ for either the solid or liquid phase of methanol, nor is it a constant for either phase. Thus, we conclude that the conditions of eqns 17.15 and 17.16 are not applicable and it is not possible to extract reliable values for either the polarizability volume or the dipole moment from this data. The data do provide valuable conceptual information about molecular motion in the condensed phases.

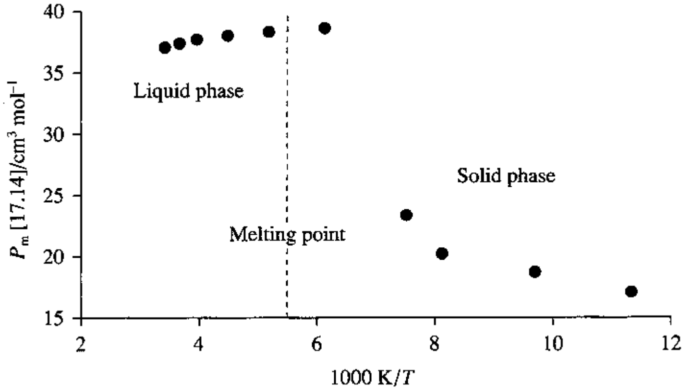


Figure 17.1

Figure 17.1 indicates that, as the temperature of liquid methanol is reduced, P_m increases less rapidly than would be expected for the linear case of thermal equilibrium of the dipole with the applied field. The progression toward lower temperatures appears to have a negative second-order component, which extends into the solid phase. The second-order regression fit for $\theta \leq -110°\text{C}$ reflects this significant non-linearity:

$$P_m/\text{cm}^3\,\text{mol}^{-1} = 31.246 + 2.3788 \times (10^3\,\text{K}/T) - 0.1904 \times (10^3\,\text{K}/T)^2, \text{ with } R^2 = 0.9914$$

This indicates that hydrogen bonding between methanol molecules is hindering molecular rotation and reducing the orientation polarization. The effect extends below the melting point with the −110°C data point exhibiting liquid-like, hindered rotation. The large decline of P_m below −110°C is interpreted as corresponding to a stronger hindrance of the dipole moment rotation but the non-constancy of P_m seems to indicate that rotational excitation is never completely eliminated.

P17.8 $$P_m = \frac{4\pi}{3}N_A\alpha' + \frac{N_A\mu^2}{9\varepsilon_0 kT}\ [17.15, \text{ with } \alpha = 4\pi\varepsilon_0\alpha']$$

Eqn 17.15 indicates that a plot of P_m against $1/T$ should be linear with a slope, $\frac{dP_m}{d(1/T)}$, equal to $\frac{N_A\mu^2}{9\varepsilon_0 k}$ and a $1/T = 0$ intercept that equals $\frac{4\pi}{3}N_A\alpha'$. Therefore, we draw up the following table and prepare a plot f P_m against $1/T$. If it is linear, we perform a linear least-squares regression fit of the plot so as to acquire the slope and intercept from which we calculate α' and μ. A suitable plot is shown in Figure 17.2.

T/K	384.3	420.1	444.7	484.1	522.0
$\frac{1000}{T/\text{K}}$	2.602	2.380	2.249	2.066	1.916
$P_m/(\text{cm}^3\,\text{mol}^{-1})$	57.4	53.5	50.1	46.8	43.1

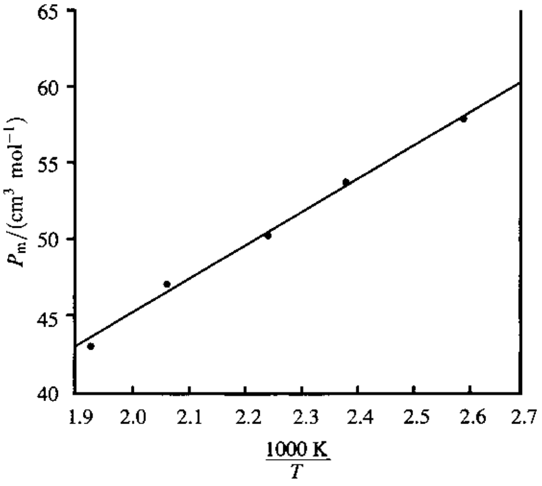


Figure 17.2

The plot of P_m against $1/T$ is linear with a regression fit that gives an intercept of 3.44 $\mathrm{cm^3\ mol^{-1}}$ (not shown in the figure), and the slope is such that $\mathrm{d}P_m/\mathrm{d}(1/T) = 2.08 \times 10^4\ \mathrm{cm^3\ mol^{-1}\ K}$. It follows that

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{3 \times (3.44\ \mathrm{cm^3\ mol^{-1}})}{4\pi \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})} = \boxed{1.36 \times 10^{-24}\ \mathrm{cm^3}}$$

$$\mu^2 = \frac{9\varepsilon_0 k}{N_A}\frac{\mathrm{d}P_m}{\mathrm{d}(1/T)}$$

$$= \left\{\frac{9 \times (8.85419 \times 10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}) \times (1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}}\right\} \times (2.08 \times 10^{-2}\ \mathrm{m^3\ mol^{-1}\ K})$$

$$= 3.80 \times 10^{-59}\ \mathrm{C^2\ m^2}$$

$$\mu = (3.80 \times 10^{-59}\ \mathrm{C^2\ m^2})^{1/2} \times \left(\frac{1\ \mathrm{D}}{3.33564 \times 10^{-30}\ \mathrm{C\ m}}\right) = \boxed{1.85\ \mathrm{D}}$$

P17.10 Let the partial charge on the carbon atom equal δe and the N-to-C distance equal l. Then,

$$\mu = \delta e l\ [17.3\mathrm{a}] \quad \text{or} \quad \delta = \frac{\mu}{el}$$

$$\delta = \frac{(1.77\ \mathrm{D}) \times (3.3356 \times 10^{-30}\ \mathrm{C\ m\ D^{-1}})}{(1.602 \times 10^{-19}\ \mathrm{C}) \times (299 \times 10^{-12}\ \mathrm{m})} = \boxed{0.123}$$

P17.12 A plot of surface tension γ against surfactant concentration [A] is shown in Figure 17.3. It is linear and the regression fit, summarized in the figure, gives a slope equal to $-25.657 \times 10^{-6}\ \mathrm{N\ m^2\ mol^{-1}}$. Solving eqn 17.50 for the surface excess $\Gamma_{[\mathrm{A}]}$ indicates that the surface excess is proportional to the bulk concentration.

$$\Gamma_{[\mathrm{A}]} = -\frac{[\mathrm{A}]}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}[\mathrm{A}]}[17.50] = -\frac{(-25.657 \times 10^{-3}\ \mathrm{N\ m^{-1}})}{(8.31447\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (293.15\ \mathrm{K})} \times \left(\frac{[\mathrm{A}]}{\mathrm{mol\ dm^{-3}}}\right)$$

$$= (1.05 \times 10^{-5}\ \mathrm{mol\ m^{-2}}) \times \left(\frac{[\mathrm{A}]}{\mathrm{mol\ dm^{-3}}}\right)$$

This equation is used to calculate the surface excess for a given value of [A]. For example, when $[\mathrm{A}] = 0.10\ \mathrm{mol\ dm^{-3}}$, $\Gamma_{[\mathrm{A}]} = (1.05 \times 10^{-5}\ \mathrm{mol\ m^{-2}}) \times (0.10) = 1.05 \times 10^{-6}\ \mathrm{mol\ m^{-2}}$.

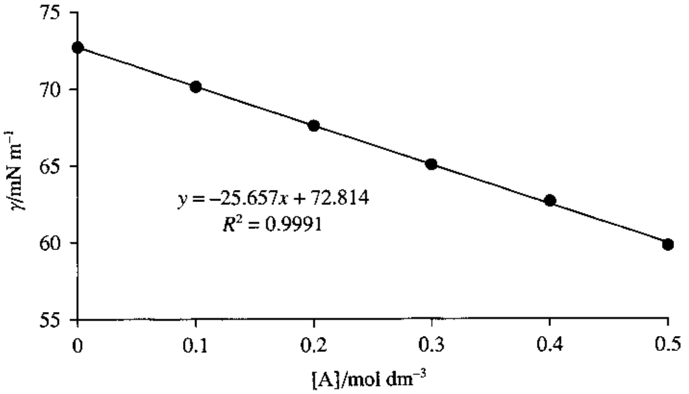


Figure 17.3

Solutions to theoretical problems

P17.14 Since the refractive index n_r and, therefore, the relative permittivity ε_r are close to 1, we infer that the dipole moment does not contribute to the molar polarization because either the gas-phase molecules are non-polar or the molecular rotational frequency is much lower than the frequency of the applied electric field, which is the case for infrared, visible, and ultraviolet radiation. Furthermore, the observation that the ratio $C \equiv \dfrac{\varepsilon_r - 1}{\varepsilon_r + 2}$ must be much less than 1 greatly simplifies mathematical manipulations.

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho N_A \alpha}{3M\varepsilon_0}\ [17.16,\ \text{Clausius–Mossotti eqn}] = \frac{\alpha p}{3\varepsilon_0 kT}\ [\rho = Mp/RT,\ \text{perfect gas}] \equiv C$$

Solving the Clausius–Mossotti eqn for ε_r gives

$$\varepsilon_r = \frac{1+2C}{1-C}, \quad \text{where} \quad C = \frac{\alpha p}{3\varepsilon_0 kT}$$
$$= (1+2C) \times (1 - C + C^2 - C^3 + \cdots)\ [\text{Taylor series expansion of } (1-C)^{-1} \text{ for } C \ll 1]$$
$$= 1 + C\ [\text{second-order and higher powers are insignificantly small and may be discarded}]$$

$$n_r = (1+C)^{1/2}\ [17.17]$$
$$= 1 + \tfrac{1}{2}C\ [\text{Taylor expansion, discard higher-order terms}]$$
$$= 1 + \frac{\alpha}{6\varepsilon_0 kT}p$$

Thus, n_r is linear in pressure p with an intercept equal to 1, which corresponds to a vacuum. The slope, $\boxed{\dfrac{\alpha}{6\varepsilon_0 kT}}$, is so small (~$10^{-4}\ \mathrm{bar^{-1}}$) that we normally consider the refractive index of a gas to be 1.00. Very sensitive measurements of the refractive index as a function of pressure may be used to find the polarizability. Solving the above equation for α gives the computational equation using measured values of temperature, pressure, and refractive index:

$$\alpha = 6\varepsilon_0 kT \times (n_r - 1)/p$$

The polarizability volume is calculated with

$$\alpha' = \alpha/4\pi\varepsilon_0 \ [17.5]$$

P17.16 Consider a single molecule surrounded by $N-1(\approx \mathrm{N})$ others in a container of volume V. The number of molecules in a spherical shell of thickness $\mathrm{d}R$ is $4\pi R^2 \times \dfrac{N}{V}\mathrm{d}R$. Molecules cannot approach more closely than the molecular diameter d so $R \geq d$ and therefore the pair interaction energy is

$$u = \int_d^\infty 4\pi R^2 \times \left(\frac{N}{V}\right) \times \left(\frac{-C_6}{R^6}\right)\mathrm{d}R = \frac{-4\pi NC_6}{V}\int_d^\infty \frac{\mathrm{d}R}{R^4} = \left(\frac{4\pi NC_6}{3V}\right) \times \left(\frac{1}{\infty^3} - \frac{1}{d^3}\right) = \frac{-4\pi NC_6}{3Vd^3}$$

The mutual pairwise interaction energy of all N molecules is $U = \frac{1}{2}Nu$ (the $\frac{1}{2}$ appears because each pair must be counted only once, i.e. A with B but not A with B and B with A). Therefore,

$$U = \boxed{\frac{-2\pi N^2 C_6}{3Vd^3}}$$

For a van der Waals gas, $\dfrac{n^2 a}{V^2} = \left(\dfrac{\partial U}{\partial V}\right)_T = \dfrac{2\pi N^2 C_6}{3V^2 d^3}$

and therefore $a = \boxed{\dfrac{2\pi N_A^2 C_6}{3d^3}}$ $[N = nN_A]$.

P17.18 The number of molecules in a volume element $\mathrm{d}\tau$ is $\mathcal{N}\mathrm{d}\tau$ where $\mathcal{N}$ is the number density. The energy of interaction of these molecules with one at a distance r is $V(r)\mathcal{N}\mathrm{d}\tau$, where $V(r)$ is the pair interaction energy, not the volume. The total interaction energy of all molecules with the one at the centre, taking into account an isotropic distribution around a centre molecule so that $\mathrm{d}\tau = 4\pi r^2 \mathrm{d}r$, is therefore $\mathcal{N}\displaystyle\int V(r)\mathrm{d}\tau = 4\pi\mathcal{N}\int_d^\infty V(r) r^2 \mathrm{d}r$, where d is the radius of a molecule. The total cohesive energy density $\mathcal{U}$, which is defined to be a positive property, is $\frac{1}{2}\mathcal{N}$ multiplied by the negative of the total interaction energy of a single molecule with the factor of $\frac{1}{2}$ assuring that the interaction of molecule A with molecule B is not counted twice. Thus,

$$\mathcal{U} = -2\pi\mathcal{N}^2 \int_d^\infty V(r)\mathrm{d}r$$

For $V(r) = -C_6/r^6$ the total energy density becomes

$$\mathcal{U} = 2\pi\mathcal{N}^2 C_6 \int_d^\infty \frac{1}{r^6} r^2 \mathrm{d}r = -\frac{2\pi\mathcal{N}^2 C_6}{3}\left[\frac{1}{r^3}\right]_d^\infty = \frac{2\pi\mathcal{N}^2 C_6}{3d^3}$$

However, the number density is related to density ρ and molar mass M by the expression

$$\mathcal{N} = N_A \rho / M$$

so

$$\mathcal{U} = \frac{2\pi}{3}\left(\frac{N_A\rho}{M}\right)^2 \frac{C_6}{d^3}$$

P17.20 As in Problem 17.19, we can write

$$\theta(v) = \begin{cases} \pi - 2\arcsin\left(\dfrac{b}{R_1 + R_2(v)}\right) & b \le R_1 + R_2(v) \\ 0 & b > R_1 + R_2(v) \end{cases}$$

where $R_2(v) = R_2 e^{-v/v^*}$. Furthermore, $R_1 = \frac{1}{2}R_2$ and $b = \frac{1}{2}R_2$.

(a) $\theta(v) = \pi - 2\arcsin\left(\dfrac{1}{1+2e^{-v/v^*}}\right)$

(The restriction $b \le R_1 + R_2(v)$ transforms into $\frac{1}{2}R_2 \le \frac{1}{2}R_2 + R_2 e^{-v/v^*}$, which is valid for all v.) This function is plotted as curve a in Figure 17.4.

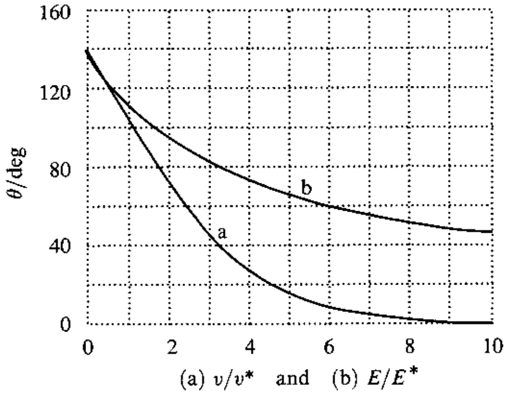


Figure 17.4

(b) The kinetic energy of approach is $E = \frac{1}{2}mv^2$, and so

$$\theta(E) = \pi - 2\arcsin\left(\frac{1}{1+2e^{-(E/E^*)^{1/2}}}\right), \quad \text{where} \quad E^* = \frac{1}{2}m(v^*)^2$$

This function is plotted as curve b in Figure 17.4.

Solutions to applications: biochemistry

P17.22 (a) The energy of induced-dipole–induced-dipole interactions can be approximated by the London formula (eqn 17.25):

$$V = -\frac{C}{r^6} = -\frac{3\alpha_1'\alpha_2'}{2r^6}\frac{I_1I_2}{I_1+I_2} = -\frac{3\alpha'^2 I}{4r^6}$$

where the second equality uses the fact that the interaction is between two of the same molecule. For two phenyl groups, we have:

$$V = -\frac{3(1.04\times10^{-29}\,\mathrm{m}^3)^2\times(5.0\,\mathrm{eV})\times(1.602\times10^{-19}\,\mathrm{J\,eV}^{-1})}{4\times(4.0\times10^{-9}\,\mathrm{m})^6} = -1.8\times10^{-26}\,\mathrm{J}$$

or $\boxed{-0.0096\,\mathrm{J\,mol}^{-1}}$.

COMMENT. A distance of 0.40 nm yields $V = -9.6\,\mathrm{kJ\,mol}^{-1}$.

(b) The potential energy is everywhere negative. We can obtain the distance dependence of the force by taking

$$F = -\frac{\mathrm{d}V}{\mathrm{d}r} = -\frac{6C}{r^7}$$

This force is everywhere attractive (i.e. it works against increasing the distance between interacting groups). The force $\boxed{\text{approaches zero as the distance becomes very large}}$; there is no finite distance at which the dispersion force is zero. (Of course, if one takes into account repulsive forces, then the net force is zero at a distance at which the attractive and repulsive forces balance.)

P17.24 (a) The dipole moment computed for *trans*-*N*-methylacetamide is

$$\mu = (3.092\,\mathrm{D})\times(3.336\times10^{-30}\,\mathrm{C\,m\,D}^{-1}) = \boxed{1.031\times10^{-29}\,\mathrm{C\,m}}$$

(semi-empirical, PM3 level, PC Spartan *Pro*™). The dipole is oriented mainly along the carbonyl group. The interaction energy of two parallel dipoles is given by eqn 17.22:

$$V = \frac{\mu_1\mu_2 f(\theta)}{4\pi\varepsilon_0 r^3},\ \text{where } f(\theta) = 1 - 3\cos^2\theta$$

and r is the distance between the dipoles and θ the angle between the direction of the dipoles and the line that joins them. The angular dependence is shown in Figure 17.5. Note that $V(\theta)$ is at a minimum for $\theta = 0°$ and 180°, while it is at a maximum for 90° and 270°.

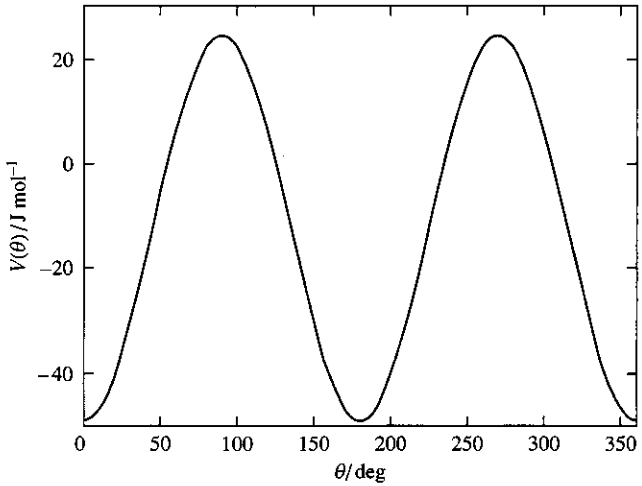


Figure 17.5

(b) If the dipoles are separated by 3.0 nm, then the maximum energy of interaction is:

$$V_{\text{max}} = \frac{(1.031\times10^{-29}\,\text{C m})^2}{4\pi(8.854\times10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})\times(3.0\times10^{-9}\,\text{m})^3} = \boxed{3.5\overline{5}\times10^{-23}\,\text{J}}$$

In molar units

$$V_{\text{max}} = (3.5\overline{5}\times10^{-23}\,\text{J})\times(6.022\times10^{23}\,\text{mol}^{-1}) = 21\,\text{J mol}^{-1} = 2.1\times10^{-2}\,\text{kJ mol}^{-1}$$

Thus, dipole–dipole interactions at this distance are $\boxed{\text{dwarfed by hydrogen-bonding interactions}}$.

However, the typical hydrogen bond length is much shorter, so this may not be a fair comparison.

P17.26 Here is a solution using MathCad.

(a) $\text{Data} := \begin{pmatrix} 7.36 & 8.37 & 8.3 & 7.47 & 7.25 & 6.73 & 8.52 & 7.87 & 7.53 \\ 3.53 & 4.24 & 4.09 & 3.45 & 2.96 & 2.89 & 4.39 & 4.03 & 3.80 \\ 1.00 & 1.80 & 1.70 & 1.35 & 1.60 & 1.60 & 1.95 & 1.60 & 1.60 \end{pmatrix}$

$\log A := (\text{Data}^T)^{\langle 0\rangle}$ $\quad S := (\text{Data}^T)^{\langle 1\rangle}$ $\quad W := (\text{Data}^T)^{\langle 2\rangle}$ $\quad \text{Mxy} := \text{augment}(S, W)$

$\text{info} := \text{regress}(\text{Mxy}, \log A, 1)$ $\quad b := \text{submatrix}(\text{info}, 3, 5, 0, 0)$ $\quad b = \begin{array}{cc} \begin{pmatrix} 0.957 \\ 0.362 \\ 3.59 \end{pmatrix} & \begin{array}{c} b_0 \\ b_1 \\ b_2 \end{array} \end{array}$

(b) $W := 1.5$ Estimate for Given/Find Solve Block

$S := 4.84$ $\quad \log A := 7.60$

Given $\quad \log A = b_0 + b_1\cdot S + b_2\cdot W$ $\quad W := \text{Find}(W)$ $\quad W = 1.362$

18

Materials 1: macromolecules and self-assembly

Answers to discussion questions

D18.2 The **freely jointed random-coil** model of a polymer chain of 'units' or 'residues' gives the simplest possibility for the conformation of the polymer that is not capable of forming hydrogen bonds or any other type of non-linkage bond. In this model, a bond that links adjacent units in the chain is free to make any angle with respect to the preceding one (see text Figures 18.3 and 18.4). We assume that the residues occupy zero volume, so different parts of the chain can occupy the same region of space. We also assume in the derivation of the expression for the probability of the ends of the chain being a distance nl apart, that the chain is compact in the sense that $n \ll N$. This model is obviously an oversimplification because a bond is actually constrained to a cone of angles around a direction defined by its neighbour and it is impossible for one section of a chain to overlap with another. Constrained angles and self-avoidance tend to swell the coil, so it is better to regard the $R_{\rm rms}$ and $R_{\rm g}$ values of a random coil as lower bounds to the actual values.

The freely jointed chain is improved by constraining each successive individual bond to a single cone of angle θ relative to its neighbour. This **constrained chain** reduces $R_{\rm rms}$ and $R_{\rm g}$ values of a freely jointed random coil by a factor of F:

$$F = \left(\frac{1-\cos\theta}{1+\cos\theta}\right)^{1/2} \quad [18.8]$$

The random-coil model also ignores the role of the solvent: a poor solvent will tend to cause the coil to tighten; a good solvent does the opposite. Therefore, calculations based on this model are best regarded as lower bounds to the dimensions of a polymer in a good solvent and as an upper bound for a polymer in a poor solvent. The model is most reliable for a polymer in a bulk solid sample, where the coil is likely to have its natural dimensions.

D18.4 The **number-average molar mass** is the value obtained by weighting each molar mass by the number of molecules with that mass (eqn 18.19).

$$\overline{M_{\rm n}} = \frac{1}{N}\sum_i N_i M_i = \langle M\rangle \, [18.19]$$

In this expression, N_i is the number of molecules of molar mass M_i and N is the total number of molecules. Measurements of the osmotic pressures of macromolecular solutions yield the number-average molar mass.

The **weight-average molar mass** is the value obtained by weighting each molar mass by the mass of each one present (eqn 18.20a).

$$\overline{M_w} = \frac{1}{m}\sum_i m_i M_i = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\langle M^2 \rangle}{\langle M \rangle} \text{ [18.20a, 18.20b]}$$

In this expression, m_i is the total mass of molecules with molar mass M_i and m is the total mass of the sample. Light-scattering experiments give the weight-average molar mass.

The ***Z*-average molar mass** is defined through the formula (eqn 18.20c).

$$\overline{M_Z} = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\langle M^3 \rangle}{\langle M^2 \rangle} \text{ [18.20c]}$$

The *Z*-average molar mass is obtained from sedimentation equilibria experiments.

The **viscosity-average molar mass** is the value obtained from measurements of the intrinsic viscosities $[\eta]$ of solutions of the macromolecule. It is obtained from the Mark–Kuhn–Houwink–Sakurada equation (18.37), where K and a are empirical values:

$$[\eta] = K\overline{M_v}^{\,a} \text{ [18.37]}, \quad \text{so} \quad \overline{M_v} = \left(\frac{[\eta]}{K}\right)^{1/a}$$

In fact, the viscosity average is also a weighted average of individual molar masses:

$$\overline{M_v} = \left(\frac{1}{m}\sum_i m_i M_i^a\right)^{1/a}$$

In terms of this equation, the weight-average molar mass corresponds to $a = 1$ and the number-average molar mass to $a = -1$. Experimentally, a is found to be in the range 0.5–1.0. Therefore, $\overline{M_v}$ is closer to $\overline{M_w}$ than to $\overline{M_n}$.

D18.6 The **protein-folding problem** involves discovery of the mechanisms for the rapidity (sometimes as short as a millisecond) and reliability by which a newly synthesized chain of amino acids folds into a three-dimensional native structure that is biologically active. The problem is three or four decades old, with recent evidence suggesting that local, secondary structures assemble first via attractive forces discussed in Chapter 17 (hydrogen bonds, London interactions, ionic interactions, disulfide links) thereafter the local structures direct optimization of the global structure. The importance of the problem is recognized by consideration of the high selectivity of a native enzymatic active site for specific substrates, which are rapidly and repetitively converted to needed products, and the need to develop health-restoring drugs that inhibit specific enzymes. Further encouragement for research in this field is provided by recent evidence that a dysfunction in protein folding contributes to nerve cell death in Alzheimer's disease.

The secondary, tertiary, and quaternary native protein structures presumably yield a global Gibbs energy minimum and therein lays the difficulty to resolving a protein-folding problem. The great flexibility of the peptide backbone means that from the equilibrium thermodynamic view there are a great many conformations that correspond to local minima in the space of all possible conformations.

This is illustrated in Figure 18.1. Many thermally accessible conformations may have similar Gibbs energy but very different associations between sections of the chain, with each set of associations leading to very different three-dimensional structures, most of which are not the native shape. The computational difficulty in predicting the native shape is complicated by the energy of interaction between the polymer chain and surrounding solvent molecules. In the aqueous environment of biological cells, the outer surface of a protein molecule is covered by a mobile sheath of water molecules, and its interior contains pockets of water molecules. These water molecules play an important role in determining the conformation that the chain adopts through hydrophobic interactions and hydrogen bonding to amino acids in the chain.

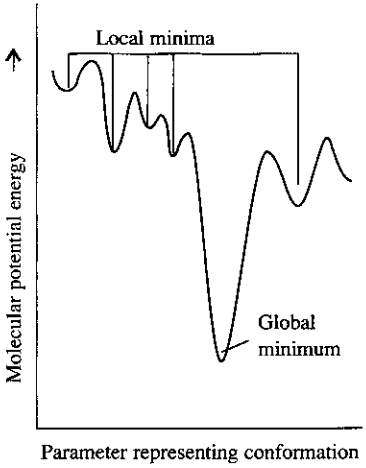


Figure 18.1

Solutions to exercises

E18.1(b) $R_{\mathrm{rms}} = N^{1/2}l\,[18.4] = (1200)^{1/2} \times (1.125\text{ nm}) = \boxed{38.97\text{ nm}}$

E18.2(b) The repeating monomer unit of polypropylene is (–CH(CH$_3$) –CH$_2$–), which has a molar mass of 42.1 g mol^{-1}. The number of repeating units, N, is therefore

$$N = \frac{M_{\text{polymer}}}{M_{\text{monomer}}} = \frac{174\text{ kg mol}^{-1}}{42.1 \times 10^{-3}\text{ kg mol}^{-1}} = 4.13 \times 10^3$$

$l = 2R(\text{C–C})$ [add half a bond length on either side of monomer]

$$R_{\mathrm{c}} = Nl\,[18.3] = 2 \times (4.13 \times 10^3) \times (1.54 \times 10^{-10}\text{ m}) = \boxed{1.27\ \mu\text{m}}$$

$$R_{\mathrm{rms}} = N^{1/2}l\,[18.4] = 2 \times (4.13 \times 10^3)^{1/2} \times (1.54 \times 10^{-10}\text{ m}) = \boxed{19.8\text{ nm}}$$

E18.3(b) For a random coil, the radius of gyration is

$$R_{\mathrm{g}} = \left(\frac{N}{6}\right)^{1/2} l\,[18.6], \quad \text{so} \quad N = 6\left(\frac{R_{\mathrm{g}}}{l}\right)^2 = 6 \times \left(\frac{18.9\text{ nm}}{0.450\text{ nm}}\right)^2 = \boxed{1.06 \times 10^4}$$

E18.4(b) The repeating monomer unit of polyethylene is ($-CH_2-CH_2-$), which has a molar mass of 28 g mol⁻¹. The number of repeating units, N, is therefore

$$N=\frac{M_{\text{polymer}}}{M_{\text{monomer}}}=\frac{85\,000\ \text{g mol}^{-1}}{28\ \text{g mol}^{-1}}=3.0\bar{4}\times10^{3}$$

$l=2R(\text{C–C})=2\times154\ \text{pm}=308\ \text{pm}$ [add half a bond length on either side of monomer]

In units of l the polymer ends are separated by the distance

$$n=\frac{15\times10^{-9}\,\text{m}}{l}=\frac{15\times10^{-9}\,\text{m}}{308\times10^{-12}\,\text{m}}=48.\bar{7}$$

Thus,

$$P=\left(\frac{2}{\pi N}\right)^{1/2}\text{e}^{-n^2/2N}\ [18.1]$$

$$=\left(\frac{2}{\pi\times3.0\bar{4}\times10^{3}}\right)^{1/2}\text{e}^{-(48.\bar{7})^2/\{2\times(3.0\bar{4}\times10^{3})\}}$$

$$=\boxed{9.8\times10^{-3}}$$

E18.5(b) We obtain (see Exercise 18.4b) $N=3.0\bar{4}\times10^{3}$ and $l=308$ pm. Thus,

$$a=\left(\frac{3}{2Nl^2}\right)^{1/2}\ [18.2]$$

$$=\left(\frac{3}{2\times(3.0\bar{4}\times10^{3})\times(308\times10^{-12}\,\text{m})^2}\right)^{1/2}=7.2\bar{1}\times10^{7}\,\text{m}^{-1}$$

The 15.00–15.10 nm range of distances between the polymer ends is very small, so we estimate that the distribution function $f(r)$ is the constant given by $f(r)=f(15.05\ \text{nm})$. The probability that the polymer ends are in this range is

$$P=f(r)\Delta r=4\pi\left(\frac{a}{\pi^{1/2}}\right)^{3}r^2\text{e}^{-a^2r^2}\Delta r\ [18.2]$$

$$=4\pi\left(\frac{7.2\bar{1}\times10^{7}\,\text{m}^{-1}}{\pi^{1/2}}\right)^{3}\times(15.05\times10^{-9}\,\text{m})^2$$

$$\times\,\text{e}^{-(7.2\bar{1}\times10^{7}\,\text{m}^{-1})^2(15.05\times10^{-9}\,\text{m})^2}\times(15.1-15.00)\times10^{-9}\,\text{m}$$

$$=\boxed{5.9\times10^{-3}}$$

E18.6(b) We obtain (see Exercise 18.4a) $N=3.0\bar{4}\times10^{3}$ and $l=308$ pm. In units of l the polymer ends are moved apart by the distance

$$n=\frac{2.0\times10^{-9}\,\text{m}}{l}=\frac{2.0\times10^{-9}\,\text{m}}{308\times10^{-12}\,\text{m}}=6.4\bar{9}$$

Thus, the molar change in conformational entropy arising from the stretch is

$$\begin{aligned}\Delta S &= -\tfrac{1}{2}RN\ln\{(1+v)^{1+v}(1-v)^{1-v}\}\,[18.7] \quad \text{with} \quad v = n/N = 6.4\overline{9}/3.0\overline{4}\times 10^{3} = 2.1\overline{3}\times 10^{-3}\\ &= -\tfrac{1}{2}\times(8.3145\ \mathrm{J\,mol^{-1}\,K^{-1}})\times(3.0\overline{4}\times 10^{3})\times\ln\{(1.0021\overline{3})^{1.0021\overline{3}}\times(0.99787)^{0.99787}\}\\ &= \boxed{-57\ \mathrm{mJ\,mol^{-1}\,K^{-1}}}\end{aligned}$$

E18.7(b) The radius of gyration for a constrained chain that has successive individual bonds constrained to a single cone of angle $\theta = 120°$ (i.e. $\cos\theta = -\tfrac{1}{2}$) is

$$R_{\mathrm{g,constrained\ coil}} = R_{\mathrm{g,random\ coil}}F \quad \text{with} \quad F = \left(\frac{1-\cos\theta}{1+\cos\theta}\right)^{1/2}[18.8] = \left(\frac{1+\frac{1}{2}}{1-\frac{1}{2}}\right)^{1/2} = \sqrt{3}$$

The percentage change in the radius of gyration on application of the constraint is

$$\begin{aligned}\left(\frac{R_{\mathrm{g,constrained\ coil}} - R_{\mathrm{g,random\ coil}}}{R_{\mathrm{g,random\ coil}}}\right)\times 100\% &= \left(\frac{R_{\mathrm{g,constrained\ coil}}}{R_{\mathrm{g,random\ coil}}} - 1\right)\times 100\% = (F-1)\times 100\%\\ &= (\sqrt{3}-1)\times 100\% = \boxed{+73.21\%}\end{aligned}$$

The percentage change in the volume on application of the constraint is

$$\begin{aligned}\left(\frac{V_{\mathrm{constrained\ coil}} - V_{\mathrm{random\ coil}}}{V_{\mathrm{random\ coil}}}\right)\times 100\% &= \left(\frac{R^{3}_{\mathrm{g,constrained\ coil}} - R^{3}_{\mathrm{g,random\ coil}}}{R^{3}_{\mathrm{g,random\ coil}}}\right)\times 100\%\\ &= \left\{\left(\frac{R_{\mathrm{g,constrained\ coil}}}{R_{\mathrm{g,random\ coil}}}\right)^{3} - 1\right\}\times 100\% = (F^{3}-1)\times 100\%\\ &= (3^{3/2}-1)\times 100\% = \boxed{+419.6\%}\end{aligned}$$

E18.8(b) $R_{\mathrm{rms}} = R_{\mathrm{rms,random\ coil}}F = N^{1/2}lF\,[18.11]$, where $F = \left(\dfrac{2l_{p}}{l} - 1\right)^{1/2}$

Thus, the percentage increase in the root-mean-square separation when the polymer persistence length is changed from l to $0.025R_{\mathrm{c}}$, with constant contour length given by the expression

$$\begin{aligned}\left(\frac{R_{\mathrm{rms}} - R_{\mathrm{rms,random\ coil}}}{R_{\mathrm{rms,random\ coil}}}\right)\times 100\% &= \left(\frac{R_{\mathrm{rms}}}{R_{\mathrm{rms,random\ coil}}} - 1\right)\times 100\% = (F-1)\times 100\%\\ &= \left\{\left(\frac{2l_{p}}{l} - 1\right)^{1/2} - 1\right\}\times 100\% = \left\{\left(\frac{2\times(0.025R_{\mathrm{c}})}{l} - 1\right)^{1/2} - 1\right\}\times 100\%\\ &= \left\{\left(\frac{2\times(0.025\times Nl)}{l} - 1\right)^{1/2} - 1\right\}\times 100\%\\ &= \{(0.50N-1)^{1/2} - 1\}\times 100\%\\ &= \boxed{+2.13\times 10^{3}\%\ \text{when}\ N = 1000}\end{aligned}$$

The percentage change in the volume as determined by the root-mean-square separation is

$$\left(\frac{V - V_{\text{rms,random coil}}}{V_{\text{rms,random coil}}}\right) \times 100\% = \left(\frac{R^3_{\text{rms}} - R^3_{\text{rms,random coil}}}{R^3_{\text{rms,random coil}}}\right) \times 100\% = (F^3 - 1) \times 100\%$$

$$= \left\{\left(\frac{2l_p}{l} - 1\right)^{3/2} - 1\right\} \times 100\% = \left\{\left(\frac{2 \times (0.025R_c)}{l} - 1\right)^{3/2} - 1\right\} \times 100\%$$

$$= \left\{\left(\frac{2 \times (0.025 \times Nl)}{l} - 1\right)^{3/2} - 1\right\} \times 100\%$$

$$= \{(0.050N - 1)^{3/2} - 1\} \times 100\% = \boxed{+3.42 \times 10^4\,\%\text{ when } N = 1000}$$

E18.9(b) In analogy to eqn 18.11 we have

$$R_g = R_{\text{g,random coil}}F = \left(\frac{N}{6}\right)^{1/2} lF, \quad \text{where} \quad F = \left(\frac{2l_p}{l} - 1\right)^{1/2}$$

Solving for l_p gives

$$l_p = \frac{l}{2}\left\{\frac{6R_g^2}{Nl^2} + 1\right\} = \frac{164\text{ pm}}{2}\left\{\frac{6 \times (3000\text{ pm})^2}{1500 \times (164\text{ pm})^2} + 1\right\} = \boxed{1.8 \times 10^4\text{ pm}}$$

E18.10(b) Each polyethene chain bond has a length $l = 154$ pm $= 0.154$ nm and the number N of chain bonds is the polymer molar mass divided by the molar mass of the repeating CH_2 unit:

$$N = \frac{M_{\text{polymer}}}{M_{CH_2}} = \frac{85\,000\text{ g mol}^{-1}}{14\text{ g mol}^{-1}} = 6.0\overline{7} \times 10^3$$

The restoring force of a freely jointed chain is

$$\mathcal{F} = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right) \qquad \nu = n/N\ [18.12a]$$

n is the displacement from equilibrium in units of l so

$$\nu = \frac{n}{N} = \frac{(2.0\text{ nm})/(0.154\text{ nm})}{6.0\overline{7} \times 10^3} = 2.1 \times 10^{-3}$$

Since $\nu \ll 1$, we use the simplified form of eqn 18.12a:

$$\mathcal{F} = \frac{nkT}{Nl}\ [18.12b] = \frac{(13.\overline{0}) \times (1.381 \times 10^{-23}\text{ J K}^{-1}) \times (298.15\text{ K})}{(6.0\overline{7} \times 10^3) \times (154 \times 10^{-12}\text{ m})} = \boxed{5.7 \times 10^{-14}\text{ N}}$$

E18.11(b) Equal amounts imply equal numbers of molecules. Hence, the number-average is (eqn 18.19)

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2}{N} = \frac{n_1M_1 + n_2M_2}{n}$$

$$= \tfrac{1}{5}(3 \times 62 + 2 \times 78)\text{ kg mol}^{-1} = \boxed{68\text{ kg mol}^{-1}}$$

and the weight average is (eqns 18.20a, 18.20b)

$$\overline{M_w}=\frac{m_1M_1+m_2M_2}{m}=\frac{n_1M_1^2+n_2M_2^2}{n_1M_1+n_2M_2}=\frac{3\times 62^2+2\times 78^2}{3\times 62+2\times 78}\ \text{kg mol}^{-1}=\boxed{69\ \text{kg mol}^{-1}}$$

E18.12(b) (a) Osmometry gives the number-average molar mass, so

$$\overline{M_n}=\frac{N_1M_1+N_2M_2}{N_1+N_2}[18.19]=\frac{n_1M_1+n_2M_2}{n_1+n_2}=\frac{\left(\frac{m_1}{M_1}\right)M_1+\left(\frac{m_2}{M_2}\right)M_2}{\left(\frac{m_1}{M_1}\right)+\left(\frac{m_2}{M_2}\right)}=\frac{m_1+m_2}{\left(\frac{m_1}{M_1}\right)+\left(\frac{m_2}{M_2}\right)}$$

$$=\frac{100\ \text{g}}{\left(\frac{25\ \text{g}}{22\ \text{kg mol}^{-1}}\right)+\left(\frac{75\ \text{g}}{7.3\overline{3}\ \text{kg mol}^{-1}}\right)}\ [\text{assume 100 g of solution}]=\boxed{8.8\ \text{kg mol}^{-1}}$$

(b) Light scattering gives the mass-average molar mass, so

$$\overline{M_w}=\frac{m_1M_1+m_2M_2}{m_1+m_2}=\frac{(25)\times(22)+(75)\times(7.33)}{100}\ \text{kg mol}^{-1}=\boxed{11\ \text{kg mol}^{-1}}$$

E18.13(b) Since the two spherical particles have different radii and different densities, their buoyancy b must be considered. The buoyancy is

$$b=1-\rho v_s\,[18.27]=1-\rho/\rho_s$$

where ρ and ρ_s are solution and solute particle densities, respectively.

Their effective masses are proportional to both b and the particle mass. The solute particle mass equals its volume multiplied by its density ρ_s so, since the solute particle has radius a, the particle mass is proportional to $a^3\rho_s$. Therefore,

$$m_{\text{eff}}\propto ba^3\rho_s$$

According to eqn 18.31, the Stoke's frictional coefficient is proportional to a and eqn 18.28 indicates that the sedimentation rate s is proportional to the effective mass and inversely proportional to the frictional coefficient. Thus,

$$s\propto\frac{ba^3\rho_s}{a}\propto ba^2\rho_s\propto(\rho_s-\rho)a^2$$

The constant of proportionality cancels when taking ratios, so the relative rates of sedimentation of the two different particles are

$$\frac{s_2}{s_1}=\left(\frac{\rho_2-\rho}{\rho_1-\rho}\right)\times\left(\frac{a_2}{a_1}\right)^2=\left(\frac{1.10-0.794}{1.18-0.794}\right)\times(8.4)^2=\boxed{56}$$

E18.14(b) $$\overline{M_n}=\frac{SfN_A}{b}[18.30]=\frac{SfN_A}{1-\rho v_s}[18.27]$$

Assuming that the solution density equals that of water at 298 K (0.9969 g cm^{-3}) and substitution of the Stokes–Einstein relationship, $f=kT/D$ [20.51], gives

$$\overline{M}_n = \frac{SRT}{(1-\rho v_s)D}$$
$$= \frac{(7.46\,\text{Sv}) \times (10^{-13}\,\text{s Sv}^{-1})(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (298.15\,\text{K})}{\{1-(996.9\,\text{kg m}^{-3}) \times (8.01\times10^{-4}\,\text{m}^3\,\text{kg}^{-1})\} \times (7.72\times10^{-11}\,\text{m}^2\,\text{s}^{-1})}$$
$$= \boxed{119\,\text{kg mol}^{-1}}$$

E18.15(b) The net force acting on the settling particle equals zero because of the balance between the gravitation pull, $m_{\text{eff}}g$, and the frictional force, fs, where s is the drift speed and the frictional coefficient, is given by Stokes's relationship $f = 6\pi a\eta$ [18.31] for a particle of radius a. Thus,

$$fs = m_{\text{eff}}g$$
$$s = \frac{m_{\text{eff}}g}{f} = \frac{bmg}{f} = \frac{(1-\rho/\rho_s)\times\{(\frac{4}{3}\pi a^3)\times\rho_s\}g}{6\pi a\eta} \text{ [18.27 and 18.31]}$$
$$= \frac{2(\rho_s-\rho)a^2g}{9\eta}$$
$$= \frac{2\times(1250\,\text{kg m}^{-3} - 1000\,\text{kg m}^{-3})\times(15.5\times10^{-6}\,\text{m})^2\times(9.8067\,\text{m s}^{-2})}{9\times(8.9\times10^{-4}\,\text{kg m}^{-1}\,\text{s}^{-1})}$$
$$= \boxed{0.15\,\text{mm s}^{-1}}$$

E18.16(b) $$\overline{M}_n = \frac{SfN_A}{b}\text{ [18.30]} = \frac{SfN_A}{1-\rho v_s}\text{ [18.27]}$$

Substitution of the Stokes–Einstein relationship, $f = kT/D$ [20.51], gives

$$\overline{M}_n = \frac{SRT}{(1-\rho v_s)D}$$
$$= \frac{(5.1\,\text{Sv})\times(10^{-13}\,\text{s Sv}^{-1})(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})\times(293.15\,\text{K})}{\{1-(0.997\,\text{g cm}^{-3})\times(0.721\,\text{cm}^3\,\text{g}^{-1})\}\times(7.9\times10^{-11}\,\text{m}^2\,\text{s}^{-1})}$$
$$= \boxed{56\,\text{kg mol}^{-1}}$$

E18.17(b) The number of solute molecules with potential energy E is proportional to $e^{-E/kT}$, hence

$$c \propto N \propto e^{-E/kT}, \quad \text{where} \quad E = \tfrac{1}{2}m_{\text{eff}}r^2\omega^2$$

Therefore, $c \propto e^{Mb\omega^2r^2/2RT}$ [$m_{\text{eff}} = bm$, $M = mN_A$] and

$$\ln c = \text{const.} + \frac{Mb\omega^2r^2}{2RT} \quad [b = 1-\rho v_s]$$

This expression indicates that the slope of a plot of $\ln c$ against r^2 is equal to $Mb\omega^2/2RT$. Therefore,

$$M = \frac{2RT\times\text{slope}}{b\omega^2} = \frac{2\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(293\,\text{K})\times(821\times10^4\,\text{m}^{-2})}{\{1-(997\,\text{kg m}^{-3})\times(7.2\times10^{-4}\,\text{m}^3\,\text{kg}^{-1})\}\times(2\pi\times1080\,\text{s}^{-1})^2}$$
$$= \boxed{3.1\times10^3\,\text{kg mol}^{-1}}$$

Solutions to problems

Solutions to numerical problems

P18.2 $S = \dfrac{s}{r\omega^2}$ [18.29]

Since $s = \dfrac{\mathrm{d}r}{\mathrm{d}t}, \dfrac{s}{r} = \dfrac{1}{r}\dfrac{\mathrm{d}r}{\mathrm{d}t} = \dfrac{\mathrm{d}\ln r}{\mathrm{d}t}$

and if we plot ln r against t, the slope gives S through

$$S = \frac{1}{\omega^2}\frac{\mathrm{d}\ln r}{\mathrm{d}t}$$

The data are as follows:

t/min	15.5	29.1	36.4	58.2
r/cm	5.05	5.09	5.12	5.19
ln(r/cm)	1.619	1.627	1.633	1.647

The points are plotted in Figure 18.2.

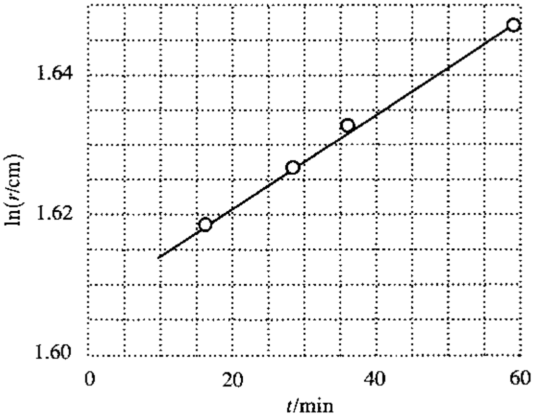


Figure 18.2

The least-squares slope is 6.62×10^{-4} min^{-1}, so

$$S = \frac{6.62 \times 10^{-4}\,\mathrm{min}^{-1}}{\omega^2} = \frac{(6.62 \times 10^{-4}\,\mathrm{min}^{-1}) \times \left(\dfrac{1\,\mathrm{min}}{60\,\mathrm{s}}\right)}{\left(2\pi \times \dfrac{4.5 \times 10^4}{60\,\mathrm{s}}\right)^2}$$

$$= 4.9\bar{7} \times 10^{-13}\,\mathrm{s} \text{ or } \boxed{5.0\,\mathrm{Sv}}$$

P18.4

$$\overline{M}_{\mathrm{w}} = \frac{2RT}{(r_2^2 - r_1^2)b\omega^2}\ln\frac{c_2}{c_1}\,[18.33] = \frac{2RT}{(r_2^2 - r_1^2)b(2\pi\nu)^2}\ln\frac{c_2}{c_1}\,[\omega = 2\pi\nu]$$

Solving for the squared rotational frequency ν and substitution of $b = 1 - \rho v_{\mathrm{s}}$ [18.27] gives

$$\begin{aligned}\nu^2 &= \frac{RT\ln(c_2/c_1)}{2\pi^2\overline{M}_{\mathrm{w}} \times (1-\rho v_{\mathrm{s}}) \times (r_2^2 - r_1^2)}\\ &= \frac{(8.3145\ \mathrm{J\ K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times \ln 5}{2\pi^2 \times (1\times 10^2\ \mathrm{kg\ mol^{-1}}) \times (1-0.75) \times (7.0^2 - 5.0^2) \times 10^{-4}\,\mathrm{m}^2}\\ &= 33\overline{67}\ \mathrm{s^{-2}}\end{aligned}$$

$$\nu = (58\ \mathrm{s^{-1}}) \times (60\ \mathrm{s\ min^{-1}}) = \boxed{3500\ \mathrm{r.p.m.}}$$

P18.6 We need to determine the intrinsic viscosity, $[\eta]$, from a plot of $((\eta/\eta_0) - 1)/(c/(\mathrm{g\ dm^{-3}}))$ against c, extrapolated to $c = 0$ as in Example 18.5. Then, from the relationship $[\eta] = K\overline{M}_{\mathrm{v}}^{\,a}$ [18.37] or $\frac{[\eta]}{\mathrm{cm^3\,g^{-1}}} = \left(\frac{K}{\mathrm{cm^3\,g^{-1}}}\right) \times \left(\frac{\overline{M}_{\mathrm{v}}}{\mathrm{g\ mol^{-1}}}\right)^a$ in conventional units with K and a from Table 18.4, the viscosity average molar mass $\overline{M}_{\mathrm{v}}$ may be calculated. η/η_0 values are determined from the times of flow using the relationship

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \times \frac{\rho}{\rho_0} \approx \frac{t}{t_0}\,[18.36]$$

noting that in the limit as c approaches 0 the approximation becomes exact.

As explored in *Self-test* 18.5, $[\eta]$ can also be determined from the limit of $(1/c)\ln(\eta/\eta_0)$ as c approaches 0. To see this, we note that, when $\eta \equiv \eta_0$,

$$\ln\frac{\eta}{\eta_0} = \ln\left(1 + \frac{\eta - \eta_0}{\eta_0}\right) = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1$$

The above relationship is exact in the limit that η coincides with η_0, which is true when $c = 0$. Hence, $[\eta]$ can also be defined as the limit of $(1/c)\ln(\eta/\eta_0)$ as $c \to 0$. We use both methods to determine the intrinsic viscosity, and thus show that they give identical results.

We draw up the following table and plot the points as shown in Figure 18.3.

$c/\mathrm{g\ dm^{-3}}$	0.000	2.22	5.00	8.00	10.00
t/s	208.2	248.1	303.4	371.8	421.3
η/η_0	—	1.192	1.457	1.786	2.024
$\dfrac{100[(\eta/\eta_0)-1]}{c/\mathrm{g\ dm^{-3}}}$	—	8.63	9.15	9.82	10.24
$\ln(\eta/\eta_0)$	—	0.1753	0.3766	0.5799	0.7048
$\dfrac{100\ln(\eta/\eta_0)}{c/\mathrm{g\ dm^{-3}}}$	—	7.89	7.52	7.24	7.05

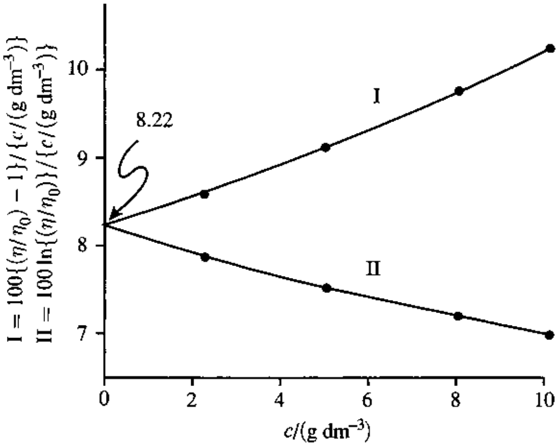


Figure 18.3

The intercept of Figure 18.3 as determined from the simultaneous extrapolation of both plots is 8.22. Hence,

$$[\eta] = 8.22 \times (0.01\ \mathrm{dm^3\ g^{-1}}) \times (10\ \mathrm{cm\ dm^{-1}})^3 = 82.2\ \mathrm{cm^3\ g^{-1}}$$

$$\overline{M}_{\mathrm{v}} = \left(\frac{[\eta]}{K}\right)^{1/a} = \left(\frac{82.2\ \mathrm{cm^3\ g^{-1}}}{9.5 \times 10^{-3}\ \mathrm{cm^3\ g^{-1}}}\right)^{1/0.74} \mathrm{g\ mol^{-1}} = \boxed{2.1 \times 10^5\ \mathrm{g\ mol^{-1}}}$$

P18.8 The Mark–Kuhn–Houwink–Sakurada equation (eqn 18.37) between $[\eta]$ and $\overline{M}_{\mathrm{v}}$ can be transformed into a linear one:

$$\begin{aligned}\ln([\eta]/\mathrm{cm^3\ g^{-1}}) &= \ln(K/\mathrm{cm^3\ g^{-1}}) + a\ln(\overline{M}_{\mathrm{v}}/\mathrm{g\ mol^{-1}})\ \text{[conventional units]}\\ &= \ln(K/\mathrm{cm^3\ g^{-1}}) + a\ln(10^3) + a\ln(\overline{M}_{\mathrm{v}}/\mathrm{kg\ mol^{-1}})\\ &= \ln(10^{3a}K/\mathrm{cm^3\ g^{-1}}) + a\ln(\overline{M}_{\mathrm{v}}/\mathrm{kg\ mol^{-1}})\end{aligned}$$

so a plot of $\ln([\eta]/\mathrm{cm^3\ g^{-1}})$ versus $\ln(\overline{M}_{\mathrm{v}}/\mathrm{kg\ mol^{-1}})$ will have a slope of a and a y-intercept of $\ln(10^{3a}K/\mathrm{cm^3\ g^{-1}})$. The transformed data and plot are shown below (Figure 18.4).

$\overline{M}_{\mathrm{v}}/\mathrm{kg\ mol^{-1}}$	10.0	19.8	106	249	359	860	1800	5470	9720	56 800
$[\eta]/\mathrm{cm^3\ g^{-1}}$	8.90	11.9	28.1	44.0	51.2	77.6	113.9	195	275	667
$\ln(\overline{M}_{\mathrm{v}}/\mathrm{kg\ mol^{-1}})$	2.30	2.99	4.66	5.52	5.88	6.76	7.509	8.61	9.18	10.90
$\ln([\eta]/\mathrm{cm^3\ g^{-1}})$	2.19	2.48	3.34	3.78	3.94	4.35	4.749	5.27	5.62	6.500

Thus, $a = \boxed{0.500}$

$$K = 10^{-3a}\mathrm{e}^{1.0028}\ \mathrm{cm^3\ g^{-1}} = \boxed{8.62 \times 10^{-2}\ \mathrm{cm^3\ g^{-1}}}$$

Solving for $\overline{M}_{\mathrm{v}}$ in the case for which $[\eta] = 100\ \mathrm{cm^3\ g^{-1}}$ yields

$$\overline{M}_{\mathrm{v}} = \left(\frac{[\eta]/\mathrm{cm^3\ g^{-1}}}{K/\mathrm{cm^3\ g^{-1}}}\right)^{1/a} \mathrm{g\ mol^{-1}} = \left(\frac{100}{8.62 \times 10^{-2}}\right)^2 \mathrm{g\ mol^{-1}} = \boxed{1.3 \times 10^3\ \mathrm{kg\ mol^{-1}}}$$

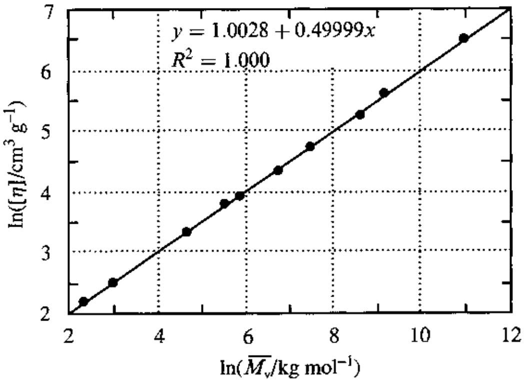


Figure 18.4

COMMENT. A solvent in which the Gibbs energy of solvent–solvent, solvent–polymer, and polymer–polymer interactions are identical is called a theta (θ) solvent. $a = \frac{1}{2}$ for theta solvents.

P18.10 $\dfrac{\Pi}{c} = \dfrac{RT}{\overline{M}_n}\left(1 + B\dfrac{c}{\overline{M}_n} + \cdots\right)$[see Section 5.5(e), Example 5.4; $\Pi = \rho g h$ and $M = \overline{M}_n$]

A plot of Π/c against c is has an intercept equal to $RT/\overline{M}_n$ at $c = 0$ and the slope at the intercept equals $BRT/\overline{M}_n^2$. Thus, $\overline{M}_n = RT/intercept$ and $B = slope \times \overline{M}_n^2/RT$. We draw up the following table and prepare the requisite plot shown in Figure 18.5.

c/g dm^{-3}	1.21	2.72	5.08	6.60
Π/c/Pa g^{-1} dm^3	111	118	129	136

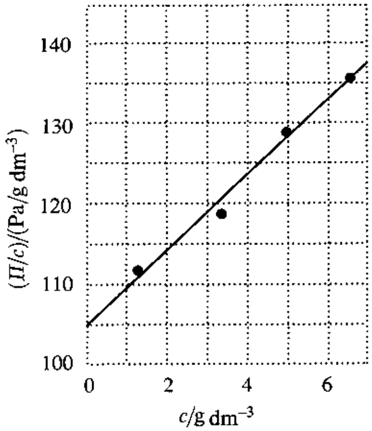


Figure 18.5

The plot of Figure 18.5 appears to be linear with a linear regression fit that gives an intercept of $105.\overline{4}$ Pa g^{-1} dm^3 and a slope of 4.64 Pa g^{-2} dm^6. It follows that

$$\overline{M}_n = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (293\ \mathrm{K})}{105.\bar{4}\ \mathrm{Pa\ kg^{-1}\ m^3}} = \boxed{23.1\ \mathrm{kg\ mol^{-1}}}$$

$$B = \frac{(23.1\ \mathrm{kg\ mol^{-1}})^2 \times (4.64\ \mathrm{Pa\ kg^{-2}\ m^6})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (293\ \mathrm{K})} = \boxed{1.02\ \mathrm{m^3\ mol^{-1}}}$$

Solutions to theoretical problems

P18.12 The fundamental vibrational frequency ν is related to the harmonic-oscillator force constant k_{force} by the expression

$$\nu = \frac{1}{2\pi}\left(\frac{k_{\text{force}}}{m}\right)^{1/2} [7.58] = \frac{1}{2\pi}\left(\frac{\mathcal{F}}{mx}\right)^{1/2} [7.57]$$

where $\mathcal{F}$ is the restoring force caused by displacement x. Substitution of $x = nl$ into the random coil model for the restoring force gives

$$\mathcal{F} = \frac{nkT}{Nl} [18.12\text{b}, n/N \ll 1] = \frac{kTx}{Nl^2}$$

Thus, with the presumption that the effective mass of Hooke's law is $m = MN^{-1}N_A^{-1}$ we find that

$$\nu = \frac{1}{2\pi l}\left(\frac{kT}{Nm}\right)^{1/2} = \boxed{\frac{1}{2\pi l}\left(\frac{RT}{M}\right)^{1/2}}$$

For the case in which $l = 154$ pm, $M = 65\ \mathrm{kg\ mol^{-1}}$, and $T = 293$ K the fundamental vibrational frequency is

$$\nu = \frac{1}{2\pi \times (154 \times 10^{-12}\ \mathrm{m})}\left\{\frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (293\ \mathrm{K})}{65\ \mathrm{kg\ mol^{-1}}}\right\}^{1/2} = \boxed{6.3\ \mathrm{GHz}}$$

The fundamental vibrational frequency has a $T^{1/2}$ dependence on temperature that reflects the thermal energy needed to establish a displacement from equilibrium. The $M^{-1/2}$ dependence indicates that a larger chain mass requires more thermal energy to establish the same displacement.

P18.14 $\mathrm{d}N = K\mathrm{e}^{-(M-\overline{M})^2/2\gamma}\,\mathrm{d}M$, where K is the constant of proportionality for the distribution.

Evaluate K by requiring that $\int \mathrm{d}N = N$.

Let $M - \overline{M} = (2\gamma)^{1/2}x$, so $\mathrm{d}M = (2\gamma)^{1/2}\mathrm{d}x$

and $N = \displaystyle\int_0^\infty K\mathrm{e}^{-(M-\overline{M})^2/2\gamma}\mathrm{d}M = K(2\gamma)^{1/2}\int_{-a}^{\infty} \mathrm{e}^{-x^2}\mathrm{d}x$, where $a = \dfrac{\overline{M}}{(2\gamma)^{1/2}}$

Note that the point $x = 0$ represents $M = \overline{M}$, and $x = -a$ represents $M = 0$. In a narrow distribution, the number of molecules with masses much different from the mean falls off rapidly as one moves away from the mean, therefore $\mathrm{d}N \approx 0$ at $M \le 0$ (that is, at $x \le -a$). Therefore,

$$N \approx K(2\gamma)^{1/2}\int_{-\infty}^{\infty} \mathrm{e}^{-x^2}\mathrm{d}x = K(2\gamma)^{1/2}\pi^{1/2}$$

Hence, $K = \dfrac{N}{(2\pi\gamma)^{1/2}}$. It then follows from turning eqn 18.19 into an integral that

$$\overline{M}_{\mathrm{n}} = \frac{1}{N}\int M\mathrm{d}N = \frac{1}{(2\pi\gamma)^{1/2}}\int_0^\infty M\,\mathrm{e}^{-(M-\overline{M})^2/2\gamma}\mathrm{d}M$$

$$= \frac{1}{(2\pi\gamma)^{1/2}}\int_0^\infty [(2\gamma)^{1/2}x + \overline{M}]\mathrm{e}^{-x^2}(2\gamma)^{1/2}\mathrm{d}x = \left(\frac{2\gamma}{\pi}\right)^{1/2}\int_{-a}^{\infty}\left(x\mathrm{e}^{-x^2} + \frac{\overline{M}}{(2\gamma)^{1/2}}\mathrm{e}^{-x^2}\right)\mathrm{d}x$$

Once again, extending the lower limit of integration to $-\infty$ adds negligibly to the integral, so

$$\overline{M}_{\mathrm{n}} \approx \left(\frac{2\gamma}{\pi}\right)^{1/2} \times \left\{1 + \left(\frac{\pi}{2\gamma}\right)^{1/2}\overline{M}\right\} = \boxed{\overline{M} + \left(\frac{2\gamma}{\pi}\right)^{1/2}}$$

P18.16 The probability that the ends of a three-dimensional freely jointed chain lie in the range r to $r + \mathrm{d}r$ is $f(r)\mathrm{d}r$, where

$$f(r) = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2\mathrm{e}^{-a^2r^2}; \quad a = \left(\frac{3}{2Nl^2}\right)^{1/2} \quad [18.2]$$

The mean nth power of the end-to-end separation is

$$\langle r^n\rangle = \int_0^\infty r^n f(r)\mathrm{d}r$$

$$\langle r^2\rangle = \int_0^\infty r^2 f(r)\mathrm{d}r = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\int_0^\infty r^4\mathrm{e}^{-a^2r^2}\mathrm{d}r$$

$$= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\frac{\Gamma(\frac{5}{2})}{2a^5}, \quad \text{where} \quad \Gamma(\tfrac{5}{2}) = \tfrac{3}{4}\pi^{1/2} \text{ [standard integral]}$$

$$= \frac{3}{2a^2} = \frac{3}{2}\left(\frac{2Nl^2}{3}\right) = \boxed{Nl^2}$$

Note: The general form of the above standard integral is

$$\int_0^\infty r^m\mathrm{e}^{-a^2r^2}\mathrm{d}r = \frac{\Gamma[(m+1)/2]}{2a^{m+1}}, \text{ where } \Gamma \text{ is the gamma function found in math handbooks}$$

P18.18 R_{g} is the radius of rotation of a point mass that has the same mass m and moment of inertia I as the object of interest. For an object that has a continuum of mass within its macroscopic boundaries:

$$I = mR_{\mathrm{g}}^2, \quad \text{where} \quad I = \int \rho R^2\mathrm{d}\tau \quad \text{and } R \text{ is the distance from the axis of rotation}$$

For a homogeneous object $\rho = m/V$ so

$$R_{\mathrm{g}}^2 = V^{-1}\int R^2\mathrm{d}\tau \text{ (The integrand is the square distance from the axis of rotation.)}$$

(a) For a solid thin disk of radius a and thickness h there are two moments of inertia, one about the disk axis ($R_{g,\perp}$, $R = r$) and another about the axis along the disk diameter ($R_{g,\parallel}$, $R = y$).

$$R_{g,\perp}^2 = (\pi a^2 h)^{-1}\int r^2 d\tau = (\pi a^2 h)^{-1}\int_{r=0}^{a}\int_{z=0}^{h}\int_{\theta=0}^{2\pi} r^3 d\theta dz dr \text{ [cylindrical coordinates]}$$

$$= (\pi a^2 h)^{-1}\int_0^a r^3 dr \times \int_0^h dz \times \int_0^{2\pi} d\theta$$

$$= \tfrac{2}{a^2}\left[\frac{r^4}{4}\right]_{r=0}^{r=a}$$

$$= \tfrac{1}{2}a^2$$

$$R_{g,\perp} = \boxed{\sqrt{\tfrac{1}{2}}a}$$

$$R_{g,\parallel}^2 = (\pi a^2 h)^{-1}\int y^2 d\tau = (\pi a^2 h)^{-1}\int_{r=0}^{a}\int_{z=0}^{h}\int_{\theta=0}^{2\pi} (r\sin\theta)^2 \times r d\theta dz dr \text{ [cylindrical coordinates]}$$

$$= (\pi a^2 h)^{-1}\int_0^a r^3 dr \times \int_0^h dz \times \int_0^{2\pi} \sin^2\theta d\theta$$

$$= (\pi a^2 h)^{-1}\left\{\left[\frac{r^4}{4}\right]_{r=0}^{r=a} \times h \times \left[\frac{\theta}{2} - \frac{\sin 2\theta}{4}\right]_{\theta=0}^{\theta=2\pi}\right\}$$

$$= \tfrac{1}{4}a^2$$

$$R_{g,\parallel} = \boxed{a/2}$$

(b) For a solid rod of radius a and length l there are two moments of inertia, one about the axis of its length ($R_{g,\parallel}$, $R = r$) and another about the axis that is perpendicular to its length ($R_{g,\perp}$, $R = z$).

$$R_{g,\parallel}^2 = (\pi a^2 l)^{-1}\int r^2 d\tau = (\pi a^2 l)^{-1}\int_{r=0}^{a}\int_{z=0}^{l}\int_{\theta=0}^{2\pi} r^3 d\theta dz dr \text{ [cylindrical coordinates]}$$

$$= (\pi a^2 l)^{-1} 2\pi l \int_0^a r^3 dr$$

$$= \tfrac{2}{a^2}\left[\frac{r^4}{4}\right]_{r=0}^{r=a}$$

$$= \tfrac{1}{2}a^2$$

$$R_{g,\parallel} = \boxed{\sqrt{\tfrac{1}{2}}a}$$

$$R_{g,\perp}^2 = (\pi a^2 l)^{-1}\int z^2 d\tau = (\pi a^2 l)^{-1}\int_{r=0}^{a}\int_{z=-l/2}^{l/2}\int_{\theta=0}^{2\pi} z^2 r d\theta dz dr \text{ [cylindrical coordinates]} = \boxed{\tfrac{1}{12}l^2}$$

$$R_{g,\perp} = \boxed{\sqrt{\tfrac{1}{12}}l}$$

(c) For a solid sphere of radius a: $V = \frac{4}{3}\pi a^3$, $\mathrm{d}\tau = r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$, and $R^2 = x^2 + y^2$.

$$R_g^2V = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{a}(x^2+y^2)r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

$$= \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{a}(r^2\sin^2\theta\cos^2\phi + r^2\sin^2\theta\sin^2\phi)r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

$$= \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{a}r^4\sin^3\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = \left\{\int_0^{2\pi}\mathrm{d}\phi\right\}\left\{\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta\right\}\left\{\int_0^{a}r^4\,\mathrm{d}r\right\}$$

$$= 2\pi\times\left\{-\cos\theta + \tfrac{1}{3}\cos^3\theta\right\}\Big|_{\theta=0}^{\theta=\pi}\times\left[\frac{r^5}{5}\right]_{r=0}^{r=a} = \frac{8\pi a^5}{15}$$

$$R_g^2 = \frac{8\pi a^5}{15V} = \frac{8\pi a^5}{15\times(\frac{4}{3}\pi a^3)} = \tfrac{2}{5}a^2$$

$$R_g = \boxed{\sqrt{\tfrac{2}{5}}a}$$

COMMENT. A common error involves using r^2 in place of the squared distance from the axis of rotation, which is actually equal to $x^2 + y^2$ not to $x^2 + y^2 + z^2 = r^2$. The common error gives the result $\sqrt{\frac{3}{5}}a$.

P18.20 The probability that the end separation is nl is [see *Further Information* 18.1(a)]:

$$P = \frac{\text{number of polymers with } N_R \text{ bonds to the right}}{\text{total number of arrangements of bonds}}$$

$$= \frac{N!/N_R!(N-N_R)!}{2^N} = \frac{N!}{\{\frac{1}{2}(N+n)\}!\{\frac{1}{2}(N-n)\}!2^N}$$

The factorials are substituted with Stirling's formula: $\ln x! \approx \ln(2\pi)^{1/2} + \frac{1}{2}(2x+1)\ln x - x$

$$\begin{aligned}
\ln P &= \ln N! - \ln\{\tfrac{1}{2}(N+n)\}! - \ln\{\tfrac{1}{2}(N-n)\}! - \ln 2^N \\
&= \ln(2\pi)^{1/2} + \tfrac{1}{2}(2N+1)\ln N - N - \ln 2^N \\
&\quad - \{\ln(2\pi)^{1/2} + \tfrac{1}{2}(N+n+1)\ln\{\tfrac{1}{2}(N+n)\} - \tfrac{1}{2}(N+n)\} \\
&\quad - \{\ln(2\pi)^{1/2} + \tfrac{1}{2}(N-n+1)\ln\{\tfrac{1}{2}(N-n)\} - \tfrac{1}{2}(N-n)\} \\
&= -\ln(2\pi)^{1/2} - \ln 2^N + \tfrac{1}{2}(2N+1)\ln N - N + \tfrac{1}{2}(N+n) + \tfrac{1}{2}(N-n) \\
&\quad - \tfrac{1}{2}(N+n+1)\ln\{\tfrac{1}{2}(N+n)\} - \tfrac{1}{2}(N-n+1)\ln\{\tfrac{1}{2}(N-n)\} \\
&= -\ln(2\pi)^{1/2} - \ln 2^N + \tfrac{1}{2}(2N+1)\ln N - \tfrac{1}{2}(N+n+1)\ln\{\tfrac{1}{2}\} - \tfrac{1}{2}(N-n+1)\ln\{\tfrac{1}{2}\} \\
&\quad - \tfrac{1}{2}(N+n+1)\ln\{N+n\} - \tfrac{1}{2}(N-n+1)\ln\{N-n\} \\
&= -\ln(2\pi)^{1/2} - \ln 2^N + \tfrac{1}{2}(2N+1)\ln N - (N+1)\ln\{\tfrac{1}{2}\} \\
&\quad - \tfrac{1}{2}(N+n+1)\ln\{N(1+\tfrac{n}{N})\} - \tfrac{1}{2}(N-n+1)\ln\{N(1-\tfrac{n}{N})\} \\
&= \ln(\tfrac{2}{\pi})^{1/2} + \tfrac{1}{2}(2N+1)\ln N - \tfrac{1}{2}(N+n+1)\ln N - \tfrac{1}{2}(N-n+1)\ln N \\
&\quad - \tfrac{1}{2}(N+n+1)\ln\{1+\tfrac{n}{N}\} - \tfrac{1}{2}(N-n+1)\ln\{1-\tfrac{n}{N}\} \\
&= \ln(\tfrac{2}{\pi})^{1/2} - \tfrac{1}{2}\ln N - \tfrac{1}{2}(N+n+1)\ln\{1+\tfrac{n}{N}\} - \tfrac{1}{2}(N-n+1)\ln\{1-\tfrac{n}{N}\} \\
&= \ln(\tfrac{2}{\pi N})^{1/2} - \tfrac{1}{2}(N+n+1)\ln\{1+\tfrac{n}{N}\} - \tfrac{1}{2}(N-n+1)\ln\{1-\tfrac{n}{N}\}
\end{aligned}$$

The final expression above for $\ln P$ confirms eqn 18.39. For a compact coil ($n/N \ll 1$) the expression simplifies using the relationship $\ln\{1+\frac{n}{N}\} = \frac{n}{N} - \frac{1}{2}(\frac{n}{N})^2 \cdots$, where third- and higher-order terms are discarded as they are negligibly small.

$$\begin{aligned}
\ln P &= \ln(\tfrac{2}{\pi})^{1/2} - \tfrac{1}{2}\ln N - \tfrac{1}{2}(N+n+1)\{\tfrac{n}{N} - \tfrac{1}{2}(\tfrac{n}{N})^2\} - \tfrac{1}{2}(N-n+1)\{-\tfrac{n}{N} - \tfrac{1}{2}(\tfrac{n}{N})^2\} \\
&= \ln(\tfrac{2}{\pi})^{1/2} - \tfrac{1}{2}(N+n+1)\{\tfrac{n}{N}\} + \tfrac{1}{2}(N-n+1)\{\tfrac{n}{N}\} \\
&\quad + \tfrac{1}{2}(N+n+1)\{\tfrac{1}{2}(\tfrac{n}{N})^2\} + \tfrac{1}{2}(N-n+1)\{\tfrac{1}{2}(\tfrac{n}{N})^2\} \\
&= \ln(\tfrac{2}{\pi N})^{1/2} - \tfrac{n^2}{N} + \tfrac{1}{2}(N+1)(\tfrac{n}{N})^2 \\
&= \ln(\tfrac{2}{\pi N})^{1/2} - \tfrac{n^2}{2N} + \tfrac{1}{2}(\tfrac{n}{N})^2
\end{aligned}$$

Since $N \gg 1$, the third term is negligibly small compared to the second term and the expression becomes

$$\ln P = \ln(\tfrac{2}{\pi N})^{1/2} - \tfrac{n^2}{2N} \quad \text{or} \quad P = (\tfrac{2}{\pi N})^{1/2}\mathrm{e}^{-n^2/2N}$$

confirming eqns 18.1 and 18.40.

P18.22 Refer to Figure 18.6.

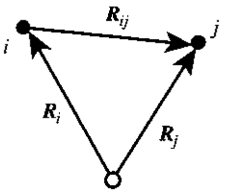


Figure 18.6

The definition of radius of gyration is

$$R_{\mathrm{g}} = \frac{1}{N}\left(\frac{1}{2}\sum_{ij} R_{ij}^2\right)^{1/2}, \quad \text{so} \quad 2N^2R_{\mathrm{g}}^2 = \sum_{ij} R_{ij}^2 = \sum_{i=1}^{N}\sum_{j=1}^{N} R_{ij}^2$$

The scalar quantity R_{ij} can be written as the dot product $\boldsymbol{R}_{ij}\cdot\boldsymbol{R}_{ij}$. If we refer all our measurements to a common origin (which we will later specify as the centre of mass), the interatomic vectors $\boldsymbol{R}_{ij}$ can be expressed in terms of vectors from the origin: $\boldsymbol{R}_{ij} = \boldsymbol{R}_j - \boldsymbol{R}_i$. (If this is not apparent, note that $\boldsymbol{R}_i + \boldsymbol{R}_{ij} = \boldsymbol{R}_j$.) Therefore,

$$\begin{aligned}
R_{\mathrm{g}}^2 &= \frac{1}{2N^2}\sum_i\sum_j (\boldsymbol{R}_j - \boldsymbol{R}_i)\cdot(\boldsymbol{R}_j - \boldsymbol{R}_i) \\
&= \frac{1}{2N^2}\sum_i\sum_j (\boldsymbol{R}_j\cdot\boldsymbol{R}_j + \boldsymbol{R}_j\cdot\boldsymbol{R}_j - 2\boldsymbol{R}_i\cdot\boldsymbol{R}_j) = \frac{1}{2N^2}\sum_i\sum_j (R_j^2 + R_i^2 - 2\boldsymbol{R}_i\cdot\boldsymbol{R}_j)
\end{aligned}$$

Look at the sums over the squared terms:

$$\sum_i\sum_j R_j^2 = \sum_i\sum_j R_i^2 = N\sum_j R_j^2$$

Hence, $R_{\mathrm{g}}^2 = \dfrac{1}{N}\sum_j R_j^2 - \dfrac{1}{N^2}\sum_i\sum_j \boldsymbol{R}_i\cdot\boldsymbol{R}_j = \dfrac{1}{N}\sum_j R_j^2 - \dfrac{1}{N^2}\sum_i \boldsymbol{R}_i\cdot\sum_j \boldsymbol{R}_j$

If we choose the origin of our coordinate system to be the centre of mass, then

$$\sum_i \boldsymbol{R}_i = \sum_j \boldsymbol{R}_j = 0 \quad \text{and} \quad R_g^2 = \frac{1}{N}\sum_j R_j^2$$

for the centre of mass is the point in the centre of the distribution such that all vectors from that point to identical individual masses sum to zero.

P18.24 Write $t = aT$, then

$$\left(\frac{\partial t}{\partial T}\right)_l = a \quad \text{and, using the result of Problem 18.23,} \left(\frac{\partial U}{\partial l}\right)_T = t - aT = 0$$

Thus, the internal energy is independent of the extension. Therefore,

$$t = aT = T\left(\frac{\partial t}{\partial T}\right)_l = \boxed{-T\left(\frac{\partial S}{\partial l}\right)_T} \text{ [Problem 18.23]}$$

and the tension is proportional to the variation of entropy with extension. Extension reduces the disorder of the chains, and they tend to revert to their disorderly (non-extended) state.

Solutions to applications: biochemistry and technology

P18.26 With concentration c in g dm^{-3} the osmotic pressure equation can be written in the form

$$\Pi = RT\left\{\frac{c}{M} + B \times \left(\frac{c}{M}\right)^2 + \cdots\right\}$$

where B is the osmotic virial coefficient in dm^3 mol^{-1}. The osmotic virial coefficient arises largely from the effect of excluded volume. If we imagine a solution of a macromolecule being built by the successive addition of macromolecules of effective radius a to the solvent, each one being excluded by the ones that preceded it, then B is the excluded volume per mole of molecules. The volume of a molecule is $v_{\text{mol}} = \frac{4}{3}\pi a^3$ but the excluded volume is determined by the smallest distance possible between centres of two molecules, which is $2a$, so the excluded volume is $\frac{4}{3}\pi(2a)^3 = 8v_{\text{mol}}$ for a pair of molecules. The volume excluded per molecule is one-half this volume or $4v_{\text{mol}}$. Thus, the osmotic virial coefficient is

$$B = 4N_A v_{\text{mol}} = \frac{16\pi}{3}N_A a^3$$

The osmotic pressure of an ideal solution is $\Pi^\circ = RTc/M$ and the percentage deviation from ideality is

$$\frac{\Pi - \Pi^\circ}{\Pi^\circ} \times 100\% = \frac{Bc}{M} \times 100\%$$

For the bushy stunt virus:

$$B = \frac{16\pi}{3}N_A(14.0 \times 10^{-9}\,\text{m})^3 = \boxed{27.7\ \text{m}^3\,\text{mol}^{-1}}$$

$$\frac{\Pi - \Pi^\circ}{\Pi^\circ} \times 100\% = \frac{(27.7\ \text{m}^3\,\text{mol}^{-1}) \times (10.0\ \text{kg m}^{-3})}{1.07 \times 10^4\ \text{kg mol}^{-1}} \times 100\% = 2.59\%$$

For haemoglobin:

$$B = \frac{16\pi}{3}N_A(3.2\times10^{-9}\,\mathrm{m})^3 = \boxed{0.33\,\mathrm{m^3\,mol^{-1}}}$$

$$\frac{\Pi - \Pi^\circ}{\Pi^\circ}\times100\% = \frac{(0.33\,\mathrm{m^3\,mol^{-1}})\times(10.0\,\mathrm{kg\,m^{-3}})}{65.5\,\mathrm{kg\,mol^{-1}}}\times100\% = 5.0\%$$

When the structure factor, $P(\theta)$, is included in eqn 18.23, the Rayleigh ratio for ideal solutions becomes

$$R(\theta) = KP(\theta)c_p\overline{M}_w\ [18.23]$$

To take deviations from ideality into account, it is common to rewrite eqn 19.23 as

$$\frac{Kc_p}{R(\theta)} = \frac{1}{P(\theta)\overline{M}_w} + \frac{2Bc_p}{\overline{M}_w^{\,2}} \quad \text{or} \quad R(\theta) = \frac{KP(\theta)c_p\overline{M}_w^{\,2}}{\overline{M}_w + 2BP(\theta)c_p}$$

where B is an empirical constant analogous to the osmotic virial coefficient and indicative of the effect of excluded volume. Thus, the percentage deviation of the Rayleigh ratio from the ideal is given by

$$\begin{aligned}\frac{R(\theta) - R^\circ(\theta)}{R^\circ(\theta)}\times100\% &= \frac{\dfrac{KP(\theta)c_p\overline{M}_w^{\,2}}{\overline{M}_w + 2BP(\theta)c_p} - KP(\theta)c_p\overline{M}_w}{KP(\theta)c_p\overline{M}_w}\times100\% \\ &= \left(\frac{\overline{M}_w}{\overline{M}_w + 2BP(\theta)c_p} - 1\right)\times100\% \\ &= \left(\frac{-2BP(\theta)c_p}{\overline{M}_w + 2BP(\theta)c_p}\right)\times100\% \\ &= \left(\frac{-2Bc_p}{\overline{M}_w + 2Bc_p}\right)\times100\%\ [\text{using } P(\theta)=1]\end{aligned}$$

We estimate that the osmotic virial coefficient, calculated above, approximates B within the Rayleigh ratio relationship.

For the bushy stunt virus:

$$\begin{aligned}\frac{R(\theta) - R^\circ(\theta)}{R^\circ(\theta)}\times100\% &= \frac{-2(27.7\,\mathrm{m^3\,mol^{-1}})\times(10.0\,\mathrm{kg\,m^{-3}})}{1.07\times10^4\,\mathrm{kg\,mol^{-1}} + (27.7\,\mathrm{m^3\,mol^{-1}})\times(10.0\,\mathrm{kg\,m^{-3}})}\times100\% \\ &= \boxed{-5.05\%}\end{aligned}$$

For haemoglobin:

$$\begin{aligned}\frac{R(\theta) - R^\circ(\theta)}{R^\circ(\theta)}\times100\% &= \frac{-2(0.33\,\mathrm{m^3\,mol^{-1}})\times(10.0\,\mathrm{kg\,m^{-3}})}{65.5\,\mathrm{kg\,mol^{-1}} + (0.33\,\mathrm{m^3\,mol^{-1}})\times(10.0\,\mathrm{kg\,m^{-3}})}\times100\% \\ &= \boxed{-9.6\%}\end{aligned}$$

P18.28 (a) We seek an expression for a ratio of scattering intensities of a macromolecule in two different conformations, a rigid rod or a closed circle. The dependence on scattering angle θ is contained in the Rayleigh ratio$R(\theta)$. The definition of this quantity, in eqn 18.22(a), gives an expression for the scattering intensity at scattering angle θ

$$I(\theta,\phi,r) = R(\theta)I_0\frac{\sin^2\phi}{r^2},$$

where ϕ is an angle between the plane of polarization of the incident beam and the plane defined by the incident and scattered beams (see text Figure 18.30). I_0 is the intensity of incident light and r the distance between sample and detector. Thus, for any given scattering angle, the ratio of scattered intensity of two conformations is the same as the ratio of their Rayleigh ratios:

$$\frac{I_{\text{rod}}}{I_{\text{cc}}} = \frac{R_{\text{rod}}}{R_{\text{cc}}} = \frac{P_{\text{rod}}}{P_{\text{cc}}}$$

The last equality stems from eqn 18.23 with the inclusion of the structure factor $P(\theta)$ of eqn 18.25, which relates the Rayleigh ratios to a number of angle-independent factors that would be the same for both conformations, and the structure factor that depends on both conformation and scattering angle. Finally, eqn 18.25 gives an approximate value of the structure factor as a function of the macromolecule's radius of gyration R_g, the wavelength of light, and the scattering angle:

$$P(\theta) \approx 1 - \frac{16\pi^2R_g^2\sin^2(\frac{1}{2}\theta)}{3\lambda^2} = \frac{3\lambda^2 - 16\pi^2R_g^2\sin^2(\frac{1}{2}\theta)}{3\lambda^2}$$

The radius of gyration of a rod of length l is

$$R_{g,\perp} = \sqrt{\tfrac{1}{12}}\,l \text{ [see Problem 18.3(b)]}$$

For a closed circle, the radius of gyration, which is the rms distance from the centre of mass [Problem 18.22], is simply the radius of a circle whose circumference is l:

$$l = 2\pi R_{\text{cc}}, \quad \text{so} \quad R_{\text{cc}} = \frac{l}{2\pi}.$$

The intensity ratio is:

$$\frac{I_{\text{rod}}}{I_{\text{cc}}} = \frac{3\lambda^2 - \frac{4}{3}\pi^2l^2\sin^2(\frac{1}{2}\theta)}{3\lambda^2 - 4l^2\sin^2(\frac{1}{2}\theta)}$$

Putting the numbers in yields:

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

(b) I would work at a detection angle at which the ratio is smallest, i.e. most different from unity, provided I had sufficient intensity to make accurate measurements. Of the angles considered in part (a), $\boxed{90°}$ is the best choice. With the help of a spreadsheet or symbolic mathematical program, the ratio can be computed for a large range of scattering angles and plotted (Figure 18.7).

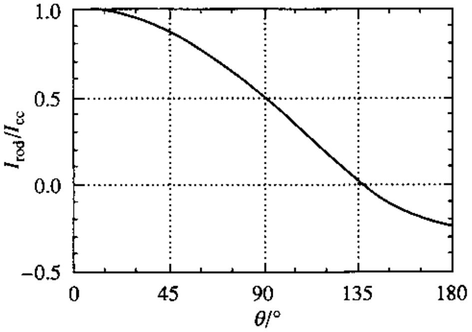


Figure 18.7

A look at the results of such a calculation shows that both the intensity ratio and the intensities themselves decrease with increasing scattering angle from 0° through 180°, that of the closed circle conformation changing much more slowly than that of the rod.

Note: The approximation used above yields negative numbers for P_{rod} at large scattering angles. This is because the approximation, which depends on the molecule being much smaller than the wavelength, is shaky at best, particularly at large angles.

P18.30 $M = \overline{M}_n$ and eqn 18.30 gives

$$M = \frac{SfN_A}{b}\,[18.30] = \frac{SfN_A}{1-\rho v_s}\,[18.27]$$

Substitution of the Stokes–Einstein relationship, $f = kT/D$ [20.51], gives

$$\begin{aligned} M &= \frac{SRT}{(1-\rho v_s)D} \\ &= \frac{(4.5\,\text{Sv})\times(10^{-13}\,\text{s Sv}^{-1})(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})\times(293.15\,\text{K})}{\{1-(998\,\text{kg m}^{-3})\times(0.75\times10^{-3}\,\text{m}^3\,\text{kg}^{-1})\}\times(6.3\times10^{-11}\,\text{m}^2\,\text{s}^{-1})} \\ &= \boxed{69\,\text{kg mol}^{-1}} \end{aligned}$$

The Stoke's relationship, $f = 6\pi a\eta$ [18.31], and the Stokes–Einstein frictional coefficient, $f = RT/D$, are equated when estimating the effective radius a.

$$f_{\text{Stoke's}} = f_{\text{Einstein–Stokes}}$$

$$6\pi a\eta = kT/D$$

$$\begin{aligned} a &= \frac{kT}{6\pi D\eta} \\ &= \frac{(1.381\times10^{-23}\,\text{J K}^{-1})\times(293.15\,\text{K})}{6\pi\times(6.3\times10^{-11}\,\text{m}^2\,\text{s}^{-1})\times(1.00\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})} = \boxed{3.4\,\text{nm}} \end{aligned}$$

P18.32 The isoelectric point is the pH at which the protein has no charge. At that point, then, its drift speed under electrophoresis, s, vanishes. Plot the drift speed against pH and extrapolate the line to $s = 0$. The plot is shown in Figure 18.8.

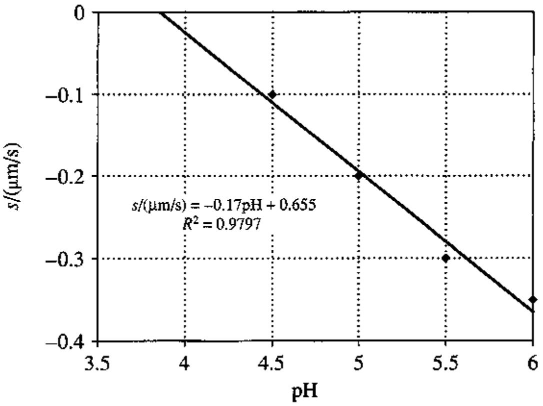


Figure 18.8

Isoelectric pH is the x-intercept on the graph, that is, the value of x at which $y = 0$. One can find this by solving the fit equation:

$$s/(\mu\text{m/s}) = -0.17\ \text{pH} + 0.655 = 0$$

$$\text{pH} = \boxed{3.8\overline{5}}$$

One could obtain the result to about ± 0.05 pH by reading the value directly from the graph.

P18.34 (a) The data are plotted in Figure 18.9. Both samples give rise to tolerably linear curves, so we estimate the melting point by interpolation using the best-fit straight line.

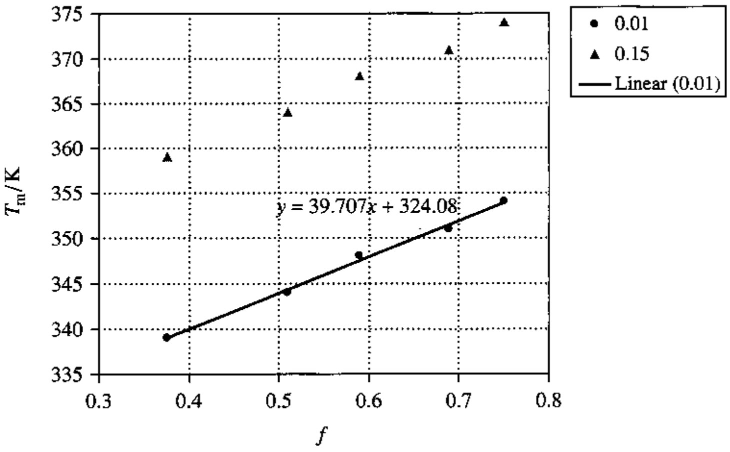


Figure 18.9

The best-fit equation has the form $T_m/\text{K} = mf + b$, and we want T_m when $f = 0.40$:

$c_{\text{salt}} = 1.0 \times 10^{-2}\ \text{mol dm}^{-3}$: $T_m = (39.7 \times 0.40 + 324)\ \text{K} = \boxed{340\ \text{K}}$

$c_{\text{salt}} = 0.15\ \text{mol dm}^{-3}$: $T_m = (39.7 \times 0.40 + 344)\ \text{K} = \boxed{360\ \text{K}}$

(b) The slopes are the same for both samples. The different concentrations of dissolved salt simply offset the melting temperatures by a constant amount with an increase in the concentration causing a higher the melting point. This behaviour is not what is typically observed with small molecules, where the presence of dissolved impurities disrupts freezing and depresses the freezing point. However, the effect of dissolved ions on DNA can be explained by considering that ions can interact with charged regions of the macromolecule, thereby reducing otherwise unfavourable intramolecular interactions. For example, if two regions bearing negative charge would have to approach each other in the absence of dissolved salts, the incorporation of a cation very close to each region and an anion in between them would turn an unfavourable interaction into a favourable one and a higher melting point. See Figure 18.10.

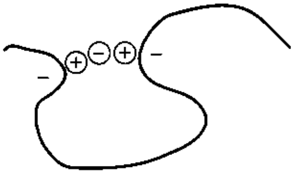


Figure 18.10

The melting points are greater at both larger fractions of G–C base pairs and at larger salt concentrations. T_m increases with the number of G–C base pairs because this pair is held together with three hydrogen bonds in the double-helical structure, whereas the A–T pair is held with two hydrogen bonds (see Section 18.5(b)). The ΔH_m contribution is greater for the G–C pair. Low salt concentrations destabilize the double helix by inadequately contributing to the attractive forces between the solution and the sugar–phosphate backbone of the double helix. This makes it easier for a base to rotate out from the centre of the double helix.

P18.36 The peaks are separated by 104 g mol^{-1}, so this is the molar mass of the repeating unit of the polymer. This peak separation is consistent with the identification of the polymer as polystyrene, for the repeating group of $CH_2CH(C_6H_5)$ (8 C atoms and 8 H atoms) has a molar mass of $8 \times (12 + 1)$ g mol^{-1} = 104 g mol^{-1}. A consistent difference between peaks suggests a pure system and points away from different numbers of subunits of different molecular weight (such as the *t*-butyl initiators) being incorporated into the polymer molecules. The most intense peak has a molar mass equal to that of *n* repeating groups plus that of a silver cation plus that of terminal groups:

$$M(\text{peak}) = nM(\text{repeat}) + M(\text{Ag}^+) + M(\text{terminal})$$

If both ends of the polymer have terminal *t*-butyl groups, then

$$M(\text{terminal}) = 2M(t\text{-butyl}) = 2(4 \times 12 + 9)\ \text{g mol}^{-1} = 114\ \text{g mol}^{-1}.$$

and $$n = \frac{M(\text{peak}) - M(\text{Ag}^+) - M(\text{terminal})}{M(\text{repeat})} = \frac{25\,578 - 108 - 114}{104} = \boxed{244}.$$

P18.38 The empirical Mark–Kuhn–Houwink–Sakurada equation [18.37] is

$$[\eta] = K\overline{M}_v^{\,a}$$

or, explicitly showing units,

$$\frac{[\eta]}{\mathrm{cm^3\,g^{-1}}} = \left(\frac{K}{\mathrm{cm^3\,g^{-1}}}\right)\times\left(\frac{\overline{M}_\mathrm{v}}{\mathrm{g\,mol^{-1}}}\right)^a = \left(\frac{10^{3a}K}{\mathrm{cm^3\,g^{-1}}}\right)\times\left(\frac{\overline{M}_\mathrm{v}}{\mathrm{kg\,mol^{-1}}}\right)^a$$

We fit the data to the above equation and obtain K and a from a regression power fitting procedure. The plot is shown in Figure 18.11 and, because of its linear appearance, both the linear and power regression fits are reported. The power fit indicates that $\boxed{a = 0.96}$, which is very close to the value of 1 of a linear fit. The value of K is

$$\frac{10^{3a}K}{\mathrm{cm^3\,g^{-1}}} = 1.75$$

$$K = 1.75\times10^{-3\times(0.95\overline{51})}\,\mathrm{cm^3\,g^{-1}} = \boxed{2.4\times10^{-3}\,\mathrm{cm^3\,g^{-1}}}$$

The value of K is significantly smaller than the value for polystyrene in benzene reported in Table 18.4 and to the value found in Problem 18.9 for polystyrene in tetrahydrofuran. The value of a is considerably larger for poly(3-hexylthiophene). The differences may indicate that P3HT in tetrahydrofuran is a stiffer polymer chain as a result of π-orbital interactions between heterocyclic rings.

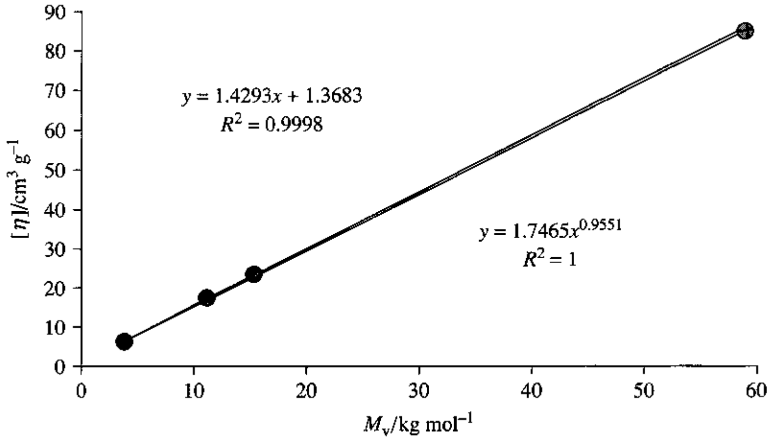


Figure 18.11

19 Solids

Answers to discussion questions

D19.2 A lattice plane is labelled by its **Miller indices** (hkl) where h, k, and l refer, respectively, to the reciprocals of the intersection distances (in units of the side lengths of the unit cell, a, b, and c) of the plane with axes that lie along the sides of a unit cell. If the reciprocal results in a fraction, the fraction is cleared by multiplication by the lowest common denominator. The notation (hkl) denotes an individual plane and the notation $\{hkl\}$ denotes a set of parallel planes.

D19.4 A **systematic absence** is an accidently forbidden reflection in the powder diffraction pattern of a lattice. The absence is caused by destructive interference due to the positions of atoms or ions giving a structure factor, and an overall amplitude of a diffracted wave, equal to zero. When the phase difference between adjacent planes in the set of planes $\{hkl\}$ is π, destructive interference between the waves diffracted from the planes can occur and this diminishes the intensity of the diffracted wave. This is illustrated in text Figure 19.21. The overall intensity of a diffracted wave from planes $\{hkl\}$ is determined from a calculation of the structure factor, F_{hkl}, which is a function of the positions (hence, of the Miller indices) and of the scattering factors of the atoms in the crystal (see eqns 19.6 and 19.7). If F_{hkl} is zero for $\{hkl\}$, that reflection is absent in the diffraction pattern (see Example 19.2). Recognition of systematic absences in a powder spectrum allows rapid identification a lattice structure. As summarized in Figure 19.23, a face-centred cubic lattice has a diffraction pattern for which h, k, and l are all even or all odd; other combinations are absent. A body-centred cubic lattice has systematic absences when the sum of h, k, and l is odd. Absences for which $(2a/\lambda) \times \sin\theta = 7^{1/2}$ or $15^{1/2}$ are characteristically absent in the pattern of a cubic P lattice (see Section 19.3(b)).

D19.6 The atomic **scattering factor**, f, describes the dependence of the magnitude of an atom's scattering of X-rays on the scattering angle θ: $f = 4\pi\int_0^\infty \rho(r)\frac{\sin kr}{kr}r^2\,\mathrm{d}r$, where $k = \frac{4\pi}{\lambda}\sin\theta$ [19.6].

The dependence on the electron density distribution in the atom, $\rho(r)$, means that heavy atoms give rise to stronger scattering than light atoms. Furthermore, since the electron distribution used to calculate the scattering factor shows no angular dependence, the scattering factor is a spherical distribution estimate that ignores the influence on scattering of partially filled valence p and d subshells. It is shown in *Justification* 19.1 that the scattering factor equals the total number of atomic, or ionic, electrons in the forward direction of scattering (i.e. $\theta = 0$). It is smaller in non-forward directions. When comparing isoelectronic atoms and ions, the less diffuse species (greater $\rho(r)$) exhibits greater scattering.

D19.8 The majority of metals crystallize in structures that can be interpreted as the closest-packing arrangements of hard spheres. These are the cubic close-packed (ccp) and hexagonal close-packed (hcp) structures in which each atom has a coordination number of 12. In these models, 74% of the volume of the unit cell is occupied by the atoms, giving a packing fraction is 0.74 in the hard-sphere model. As indicated in Table 19.2 most of the remaining metallic elements crystallize in the body-centered cubic (cubic-I or bcc, coordination number of 8) arrangement, which is not too much different from the close-packed structures in terms of the efficiency of the use of space. The bcc packing fraction is 0.68. Polonium is an exception as α-Po has the cubic-P (primitive cubic, coordination number of 6) lattice structure, which has a packing fraction of 0.52. (See the solution to Exercise 19.21a for a derivation of the packing fractions in cubic systems.)

If atoms were truly hard spheres, we would expect that all metals would crystallize in either the ccp or hcp close-packed structures. The fact that a significant number crystallize in other structures is evidence for interactions between the atoms. For elemental metallic solids the effect of ionic and covalent character in bonding between atoms may prevent close packing by directing non-close packing bond angles and lengths. Bonding draws atoms together and in doing so, reduces the coordination number below the 12 of close packing by squeezing out non-bonded atoms of neighbouring layers.

D19.10 Semiconductors generally have lower electrical conductivity than most metals. Additionally, the conductivity of semiconductors increases as the temperature is raised, whereas that of metals decreases. The difference occurs because of the relative balance between the excitation of electrons into electrical conductance and the scattering of electrons off the conductance path by collisions with vibrating atoms. The scattering process predominates with increasing temperature of a metal. The excitation process predominates for the semiconductor.

The electronic structure of solids consists of allowed energy bands. The highest energy band of a metal is partially filled. Being approximately filled to the Fermi level only, there is no gap of forbidden energies for excitation. It is easy to promote electrons from the filled level in which all random vector momentums are occupied to levels in which there is a preferred vector momentum. This provides high electrical conductivity. The energy difference between the top of the band and the Fermi level helps to explain their appearance. If sufficiently wide, all incident visible light can be both absorbed and emitted. This gives many metals their shiny, 'silver' luster. A narrow width may result in colour as a range of visible frequencies are preferentially emitted. An example is the reddish colour of copper.

Semiconductors have a band gap, E_g, between a filled valence band and an approximately unfilled conductance band above it. Significant energy is needed to promote electrons to the conductance band. The energy may be provided thermally with the application of higher temperature, with electromagnetic radiation of frequency above $\nu_{\min} = E_g/h$, or with an applied voltage. The visual appearance of a semiconductor is approximated with $\nu_{\min}$. For example, electromagnetic radiation with more energy than green light is absorbed by cadmium sulfide, so the yellow, orange, and red visible light are predominately reflected and seen as a yellow-orange colour by an observer. See the *Brief illustration* in Section 19.10(b).

D19.12 The Davydov splitting in the exciton bands of a crystal can be understood by considering the allowed transitions of interacting dipoles of neighbouring molecules. As shown in text Figure 19.58, the parallel alignment of transition dipoles is energetically unfavourable, and the exciton absorption is shifted to higher energy (blue shifted) than in the isolated molecules. However, a head-to-tail alignment is energetically favourable, and the transition occurs at a lower frequency (red shifted) than in the isolated molecules. Transition dipoles are rarely in a single parallel or head-to-tail alignment. As shown in text Figure 19.59, transition moments may often be either energetically favoured or energetically unfavoured. These crystals exhibit both the blue shifted and the red shifted band and the separation of the bands is the **Davydov or exciton splitting**.

Solutions to exercises

E19.1(b) $(\frac{1}{2},0,\frac{1}{2})$ is the midpoint of a face. All face midpoints are alike, including $\boxed{(\frac{1}{2},\frac{1}{2},0) \text{ and } (0,\frac{1}{2},\frac{1}{2})}$. There are six faces to each cube, but each face is shared by two cubes. So other face midpoints can be described by one of these three sets of coordinates on an adjacent unit cell.

E19.2(b) Taking reciprocals of the coordinates yields $(1,\frac{1}{3},-1)$ and $(\frac{1}{2},\frac{1}{3},\frac{1}{4})$, respectively. Clearing the fractions yields the Miller indices $\boxed{(31\bar{3}) \text{ and } (643)}$.

E19.3(b) The distance between planes in a cubic lattice is $d_{hkl}=\dfrac{a}{(h^2+k^2+l^2)^{1/2}}$ [19.2].

$$d_{121}=\frac{523\text{ pm}}{(1^2+2^2+1^2)^{1/2}}=\boxed{214\text{ pm}}$$

$$d_{221}=\frac{523\text{ pm}}{(2^2+2^2+1)^{1/2}}=\boxed{174\text{ pm}}$$

$$d_{244}=\frac{523\text{ pm}}{(2^2+4^2+4^2)^{1/2}}=\boxed{87.2\text{ pm}}$$

E19.4(b) $\lambda=2d\sin\theta\ [19.5]=2\times(128.2\text{ pm})\times\sin 19.76°=\boxed{86.7\text{ pm}}$

E19.5(b) Combining the Bragg law with Miller indices yields, for a cubic cell

$$\sin\theta_{hkl}=\frac{\lambda}{2a}(h^2+k^2+l^2)^{1/2}$$

In a face-centred cubic lattice, *h*, *k*, and *l* must be all odd or all even (see Figure 19.23 of text). So the first three reflections would be from the (111), (200), and (220) planes. In an fcc cell, the face diagonal of the cube is $4R$, where R is the atomic radius. The relationship of the side of the unit cell to R is therefore

$$(4R)^2=a^2+a^2=2a^2,\quad \text{so}\quad a=\frac{4R}{\sqrt{2}}$$

Now, we evaluate

$$\frac{\lambda}{2a}=\frac{\lambda}{4\sqrt{2}R}=\frac{154\text{ pm}}{4\sqrt{2}(144\text{ pm})}=0.189$$

We set up the following table:

hkl	sin *θ*	*θ*/°	2*θ*/°
111	0.327	19.1	$\boxed{38.2}$
200	0.378	22.2	$\boxed{44.4}$
220	0.535	32.3	$\boxed{64.6}$

E19.6(b) In a circular camera, the distance between adjacent lines is $D = R\Delta(2\theta)$, where R is the radius of the camera (distance from sample to film) and θ is the diffraction angle in radians. Combining these quantities with the Bragg law ($\lambda = 2d\sin\theta$, relating the glancing angle to the wavelength and separation of planes), we get

$$D = 2R\Delta\theta = 2R\Delta\left(\sin^{-1}\frac{\lambda}{2d}\right)$$

$$= 2(5.74\text{ cm}) \times \left(\sin^{-1}\frac{96.035\text{ pm}}{2(82.3\text{ pm})} - \sin^{-1}\frac{95.401\text{ pm}}{2(82.3\text{ pm})}\right) = \boxed{0.054\text{ cm}}$$

E19.7(b) *Justification* 9.1 demonstrates that the scattering factor in the forward direction equals the number of electrons in the atom or simple ion. Consequently, $\boxed{f_{\mathrm{Mg}^{2+}} = 10}$.

E19.8(b) The volume of a hexagonal unit cell is given by $V = hA$, where h is the height of the cell and A is the area of the hexagonal face, which is shown in Figure 19.1. A equals 12 times the right triangular area, shown in the figure, defined by the hexagonal face of segment length a.

$$A = 12\{\tfrac{1}{2}r \times (a/2)\} = 3ar = 3a \times (a\cos 30°) = 3a^2\sqrt{3}/2$$

$$V = Ah = 3a^2h\sqrt{3}/2$$

$$= 3 \times (1692.9 \times 10^{-12}\text{ m})^2 \times (506.96 \times 10^{-12}\text{ m}) \times \sqrt{3}/2$$

$$= 3.7747 \times 10^{-27}\text{ m}^3 = \boxed{3.7747\text{ nm}^3}$$

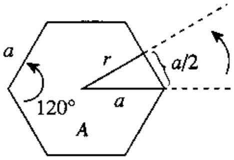


Figure 19.1

E19.9(b) The volume of an orthorhombic unit cell is

$$V = abc = (589\text{ pm}) \times (822\text{ pm}) \times (798\text{ pm})$$

$$= \frac{3.86 \times 10^{8}\text{ pm}^3}{(10^{10}\text{ pm cm}^{-1})^3} = 3.86 \times 10^{-22}\text{ cm}^3$$

The mass per formula unit is

$$m = \frac{135.01\ \text{g mol}^{-1}}{6.02214 \times 10^{23}\ \text{mol}^{-1}} = 2.2419 \times 10^{-22}\ \text{g}$$

The density ρ is related to the mass m per formula unit, the volume V of the unit cell, and the number N of formula units per unit cell as follows

$$\rho = \frac{Nm}{V}, \quad \text{so} \quad N = \frac{\rho V}{m} = \frac{(2.9\ \text{g cm}^{-3}) \times (3.86 \times 10^{-22}\ \text{cm}^3)}{2.24 \times 10^{-22}\ \text{g}} = \boxed{5}$$

A more accurate density, then, is

$$\rho = \frac{5 \times (2.24 \times 10^{-22}\ \text{g})}{3.86 \times 10^{-22}\ \text{cm}^3} = \boxed{2.90\ \text{g cm}^{-3}}$$

E19.10(b)

$$d_{hkl} = \left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2\right]^{-1/2} \quad [19.3]$$

$$d_{411} = \left[\left(\frac{3}{679}\right)^2 + \left(\frac{2}{879}\right)^2 + \left(\frac{2}{860}\right)^2\right]^{-1/2}\ \text{pm} = \boxed{182\ \text{pm}}$$

E19.11(b) Since the reflection at 17.7° is (111), we know that

$$d_{111} = \frac{\lambda}{2\sin\theta}\ [19.5] = \frac{137\ \text{pm}}{2 \times \sin 17.7°} = 225\ \text{pm}$$

and hence, since $d_{111} = \dfrac{a}{(1^2 + 1^2 + 1^2)^{1/2}}\ [19.2] = \dfrac{a}{3^{1/2}}$ for a cubic unit cell, it follows that

$$a = (3^{1/2}) \times (225\ \text{pm}) = 389\ \text{pm}$$

The indices of the other reflections are obtained from

$$(h^2 + k^2 + l^2) = \left(\frac{a}{d_{hkl}}\right)^2\ [19.2] = \left(\frac{2a\sin\theta}{\lambda}\right)^2\ [19.5]$$

We draw up the following table:

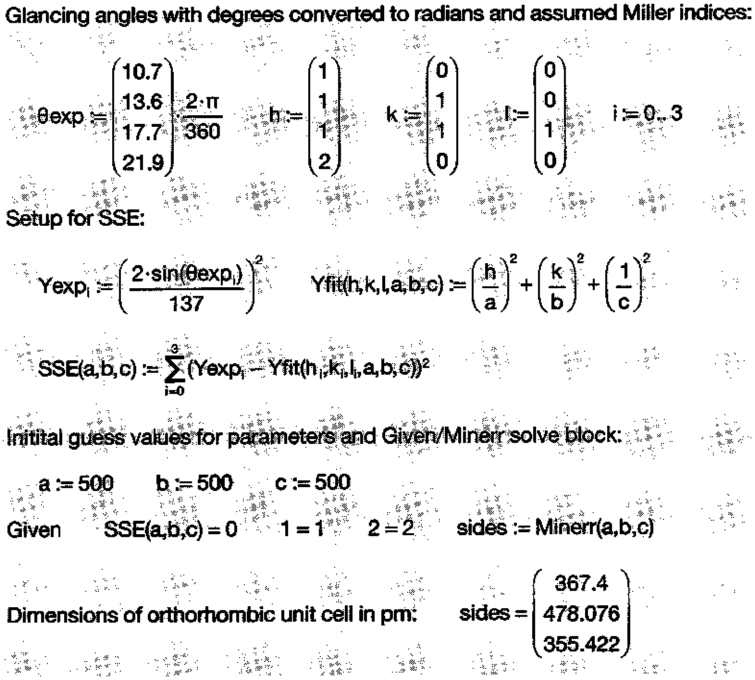
θ/°	$\left(\dfrac{2a\sin\theta}{\lambda}\right)^2$	$h^2 + k^2 + l^2$	(hkl)	a/pm
10.7	1.11	1(?)	$\boxed{(100)}$	369
13.6	1.78	2(?)	$\boxed{(110)}$	412
17.7	2.98	3	(111)	390
21.9	4.49	4(??)	$\boxed{(200)}$	367

The calculated values reported in the second table column give cause for concern because they are not very close to integer values. The third column rounds the second column off to the nearest integer to give values of $h^2 + k^2 + l^2$ for which we have little confidence. If the third column values are correct, the reflections are those of the fourth column and the unit cell is $\boxed{\text{cubic P}}$ (primitive unit cell, see text Figure 19.23). The final column values are obtained from

$$a = \left(\frac{\lambda}{2\sin\theta}\right) \times (h^2 + k^2 + l^2)^{1/2}$$

and averaged to $a = 385$ pm with a standard deviation of 21 pm (5%). Having expected a standard deviation of about 1%, the variation in a reinforces concern about either the data or the analysis. Something could be wrong with the data or, perhaps, the cubic cell assumption is wrong.

The exercise can be expanded as a small project by assuming that the glancing angle data is good but the unit cell is orthorhombic. We take the Miller indices to be (100), (110), (111), and (200) and the project is to find the unit cell dimensions a, b, c using a fitting procedure that minimizes the sum of the squares of errors (SSE). We will perform the fit with Mathcad as its Given/Minerr solve block is very convenient for the minimization of SSE. The key is recognition that eqns 19.3 and 19.5 provide two expressions for $Y = 1/d_{hkl}^2$. One expression is $Y_{\text{fit}} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$ for each data point where the parameters a, b, and c are determined by the minimization fit. The other expression is $Y_{\text{exp}} = \left(\frac{2\sin\theta}{\lambda}\right)^2$ for each data point. We must adjust the parameters a, b, and c so that the function $SSE = \sum_{i}^{\text{all data}} (Y_{\text{exp}} - Y_{\text{fit}})_i^2$ is minimized. Here is the Mathcad worksheet:



Glancing angles with degrees converted to radians and assumed Miller indices:

$$\theta\text{exp} := \begin{pmatrix}10.7\\13.6\\17.7\\21.9\end{pmatrix} \cdot \frac{2\cdot\pi}{360} \qquad h := \begin{pmatrix}1\\1\\1\\2\end{pmatrix} \qquad k := \begin{pmatrix}0\\1\\1\\0\end{pmatrix} \qquad l := \begin{pmatrix}0\\0\\1\\0\end{pmatrix} \qquad i := 0..3$$

Setup for SSE:

$$\text{Yexp}_i := \left(\frac{2\cdot\sin(\theta\text{exp}_i)}{137}\right)^2 \qquad \text{Yfit}(h,k,l,a,b,c) := \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

$$\text{SSE}(a,b,c) := \sum_{i=0}^{3} \left(\text{Yexp}_i - \text{Yfit}(h_i,k_i,l_i,a,b,c)\right)^2$$

Initial guess values for parameters and Given/Minerr solve block:

$a := 500 \qquad b := 500 \qquad c := 500$

Given $\quad \text{SSE}(a,b,c) = 0 \qquad 1 = 1 \qquad 2 = 2 \qquad \text{sides} := \text{Minerr}(a,b,c)$

Dimensions of orthorhombic unit cell in pm: $\quad \text{sides} = \begin{pmatrix}367.4\\478.076\\355.422\end{pmatrix}$

Glancing angles of fit in degrees:

$$\theta\mathrm{fit}_i := \mathrm{asin}\left(\frac{137\cdot \mathrm{Yfit}(h_i,k_i,l_i,\mathrm{sides}_0,\mathrm{sides}_1,\mathrm{sides}_2)^{1/2}}{2}\right)\cdot\frac{360}{2\cdot\pi}\qquad \theta\mathrm{fit} = \begin{pmatrix} 10.745 \\ 13.6 \\ 17.7 \\ 21.894 \end{pmatrix}$$

The last line of the worksheet indicates that the glancing angles found by the fit procedure are in very good agreement with the experimental glancing angles. The fit gives $a = 367$ pm, $b = 478$ pm, and $c = 355$ pm.

E19.12(b) $\theta_{hkl} = \arcsin\dfrac{\lambda}{2d_{hkl}}$ [from eqn 19.5] $= \arcsin\left\{\dfrac{\lambda}{2}\left[\left(\dfrac{h}{a}\right)^2+\left(\dfrac{k}{b}\right)^2+\left(\dfrac{l}{c}\right)^2\right]^{1/2}\right\}$ [from eqn 19.3]

$$\theta_{100} = \arcsin\left\{\frac{83.42}{2}\left[\left(\frac{1}{574.1}\right)^2+\left(\frac{0}{796.8}\right)^2+\left(\frac{0}{495.9}\right)^2\right]^{1/2}\right\} = \boxed{4.166^\circ}$$

$$\theta_{010} = \arcsin\left\{\frac{83.42}{2}\left[\left(\frac{0}{574.1}\right)^2+\left(\frac{1}{796.8}\right)^2+\left(\frac{0}{495.9}\right)^2\right]^{1/2}\right\} = \boxed{3.001^\circ}$$

$$\theta_{111} = \arcsin\left\{\frac{83.42}{2}\left[\left(\frac{1}{574.1}\right)^2+\left(\frac{1}{796.8}\right)^2+\left(\frac{1}{495.9}\right)^2\right]^{1/2}\right\} = \boxed{7.057^\circ}$$

E19.13(b) All of the reflections present have $h+k+l$ even, and all of the even $h+k+l$ are present. The unit cell, then, is $\boxed{\text{body-centred cubic}}$. See Figure 19.23 of text.

E19.14(b) The structure factor is given by

$$F_{hkl} = \sum_i f_i e^{i\phi_i}, \quad \text{where} \quad \phi_i = 2\pi(hx_i + ky_i + lz_i)\ [19.7]$$

All eight of the vertices of the cube are shared by eight cubes, so each vertex has a scattering factor of $f/8$.

The coordinates of all vertices are integers, so the phase ϕ is a multiple of 2π and $e^{i\phi} = 1$. The body-centre point belongs exclusively to one unit cell, so its scattering factor is f. The phase is

$$\phi = 2\pi(\tfrac{1}{2}h + \tfrac{1}{2}k + \tfrac{1}{2}l) = \pi(h+k+l)$$

When $h+k+l$ is even, ϕ is a multiple of 2π and $e^{i\phi} = 1$; when $h+k+l$ is odd, ϕ is π plus a multiple of 2π and $e^{i\phi} = -1$. So, $e^{i\phi} = (-1)^{h+k+l}$ and

$$F_{hkl} = 8(f/8)(1) + f(-1)^{h+k+l}$$

$$= \boxed{2f \text{ for } h+k+l \text{ even} \quad \text{and} \quad 0 \text{ for } h+k+l \text{ odd}} \text{ for the body-centred cubic lattice}$$

E19.15(b) The electron density is given by

$$\rho(r) = \frac{1}{V}\sum_{hkl} F_{hkl}\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)} \; [19.8]$$

The component along the x direction is

$$\rho(x) = \frac{1}{V}\sum_{h} F_h\mathrm{e}^{-2\pi\mathrm{i}hx}$$

Using the data of this problem, we sum from $h = -9$ to $+9$ and use the relationship $F_h = F_{|h|}$. The following Mathcad worksheet computation of $\rho(1.0)$ uses unit volume. Figure 19.2 shows $\rho(x)$ with x in units of a. High electron density is indicated at the ends of unit cell edge (i.e. at the vertices).

$$F := \begin{pmatrix} 10 \\ 10 \\ 4 \\ 4 \\ 6 \\ 6 \\ 8 \\ 8 \\ 10 \\ 10 \end{pmatrix}$$

$$\rho(x) := \sum_{h=-9}^{9} \left(F_{|h|} \cdot e^{-2\cdot\pi\cdot i\cdot h\cdot x}\right)$$

$$\rho(1.0) = 142$$

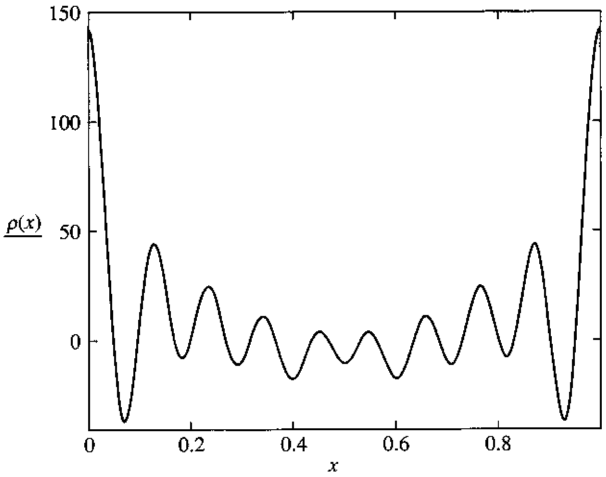


Figure 19.2

E19.16(b) Using the information of Exercise 19.15b, the Mathcad worksheet computation of $P(1.0)$ is performed with eqn 19.9.

$$F := \begin{pmatrix} 10 \\ 10 \\ 4 \\ 4 \\ 6 \\ 6 \\ 8 \\ 8 \\ 10 \\ 10 \end{pmatrix} \qquad P(x) := \sum_{h=-9}^{9} \left[(F_{h})^2 \cdot e^{-2\cdot\pi\cdot i\cdot h\cdot x} \right]$$

$$P(1.0) = 1.164 \times 10^3$$

The Patterson synthesis $P(x)$ of Figure 19.3 with x in units of a shows that atoms represented by this data are separated by $1a$ unit along the x-axis.

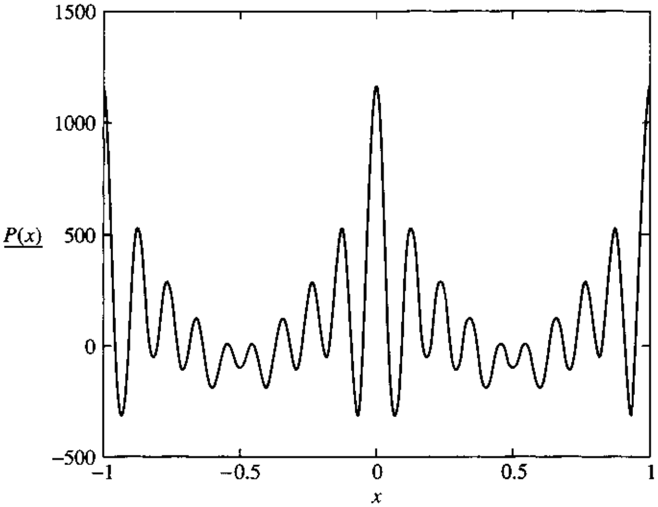


Figure 19.3

E19.17(b) Draw points corresponding to the vectors joining each pair of atoms. Heavier atoms give more intense contributions than light atoms. Remember that there are two vectors joining any pair of atoms ($\overrightarrow{AB}$ and $\overleftarrow{AB}$); don't forget the AA zero vectors for the centre point of the diagram. See Figure 19.4 for C_6H_6.

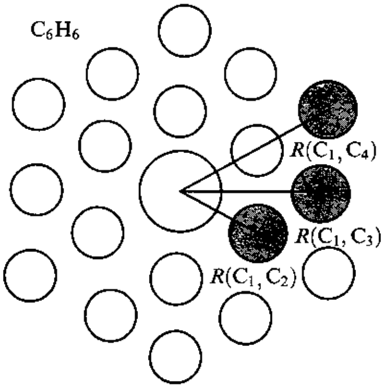


Figure 19.4

E19.18(b) By the de Broglie relationship: $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

Hence, $$v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(1.675 \times 10^{-27}\,\mathrm{kg}) \times (105 \times 10^{-12}\,\mathrm{m})} = \boxed{3.77\ \mathrm{km\,s^{-1}}}$$

E19.19(b) As discussed in text Example 19.4 the wavelength of a thermal neutron is

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{[(1.675 \times 10^{-27}\,\mathrm{kg}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (380\,\mathrm{K})]^{1/2}} = \boxed{224\ \mathrm{pm}}$$

E19.20(b) There are two smaller (black) triangles to each larger (brown) triangle. Let the area of the larger triangle be A and the area of the smaller triangle be a. Since $b = \frac{1}{2}B$(base) and $h = \frac{1}{2}H$(height), $a = \frac{1}{4}A$. The black space is then $2NA/4$, for N of the larger triangles. The total space is then $(NA + \frac{NA}{2}) = 3NA/2$. Therefore, the fraction filled is $NA/(3NA/2) = \boxed{\frac{2}{3}}$.

E19.21(b) The diagonal of the face that has a lattice point in its centre is equal to $4r$, where r is the radius of the atom. The relationship between this diagonal and the edge length a is

$$4r = a\sqrt{2}, \quad \text{so} \quad a = 2\sqrt{2}r$$

The volume of the unit cell is a^3, and each cell contains two atoms. (Each of the eight vertices is shared among eight cells; each of the two face points is shared by two cells.) So the packing fraction is

$$\frac{2V_{\text{atom}}}{V_{\text{cell}}} = \frac{2(4/3)\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{3(2)^{3/2}} = \boxed{0.370}$$

E19.22(b) Consider the eightfold coordination shown in Figure 19.5, where we take the smallest distance between the larger hard-spheres at corners to be $2R$ and the closest approach of a large and small hard sphere to be $R + r$. This lattice gives the minimum value of the **radius ratio**, $\gamma = r/R$ [19.12]. The body diagonal of the cube is $a\sqrt{3}$. Hence

$$a\sqrt{3} = 2R + 2r \quad \text{or} \quad \sqrt{3}R = R + r\,[a = 2R] \quad \text{or} \quad \sqrt{3} = 1 + \gamma$$

$$\gamma = \sqrt{3} - 1 = \boxed{0.73205}$$

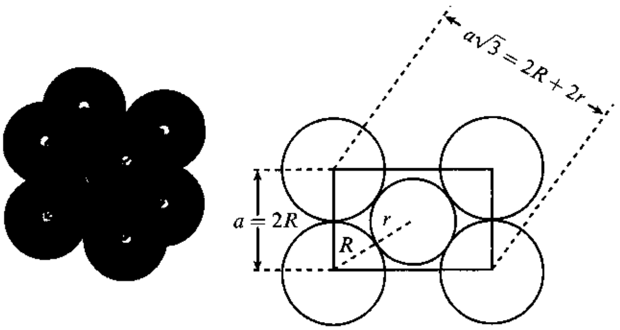


Figure 19.5

E19.23(b) The radius ratios determined in Exercises 19.22a and 19.22b correspond to the smallest value of the radius of the interior anion, since any smaller value would tend to bring the anions closer and increase their interionic repulsion and at the same time decrease the attractions of cation and anion.

(a) For sixfold coordination: $\dfrac{r_{\text{anion}}}{R_{\text{cation}}} = 0.414$ [Exercise 19.22a]

$$r_{\text{anion}} = (0.414) \times (138\text{ pm})\,[\text{Table 19.3}] = \boxed{57.1\text{ pm}}$$

(b) For eightfold coordination: $\dfrac{r_{\text{anion}}}{R_{\text{cation}}} = 0.732$ [Exercise 19.22b]

$$r_{\text{anion}} = (0.732) \times (151\text{ pm}) = \boxed{111\text{ pm}}$$

E19.24(b) The volume change is a result of two counteracting factors: different packing fractions f and different radii r. Let V and v be the unit cell volume and the atomic hard-sphere volume, respectively. $v \propto r^3$, so the ratio of unit cell volumes is given by

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{f_{\text{hcp}}}{f_{\text{bcc}}} \times \frac{v_{\text{bcc}}}{v_{\text{hcp}}} = \frac{f_{\text{hcp}}}{f_{\text{bcc}}} \times \frac{r_{\text{bcc}}^3}{r_{\text{hcp}}^3}$$

Since the packing fractions are

$$f_{\text{hcp}} = 0.7405 \quad \text{and} \quad f_{\text{bcc}} = 0.6802 \;[\textit{Justification}\text{ 19.3 and Exercise 19.21a}],$$

the unit cell volume ratio for iron is

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{0.7405}{0.6802} \times \frac{(122)^3}{(126)^3} = 0.988$$

Hence, there is a $\boxed{\text{contraction}}$ of 1.2% when iron transforms from hcp to bcc. (Actually, the data are not precise enough to be sure of this. 122 could mean 122.49 and 126 could mean 125.51, in which case an expansion would occur.)

E19.25(b) The lattice enthalpy is the difference in enthalpy between an ionic solid and the corresponding isolated ions. In this exercise, it is the enthalpy corresponding to the process

$$\text{MgBr}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{Br}^-(\text{g})$$

The standard lattice enthalpy can be computed from the standard enthalpies given in the exercise by considering the formation of $\text{MgBr}_2(\text{s})$ from its elements as occurring through the following steps: sublimation of Mg(s), removing two electrons from Mg(g), vaporization of $\text{Br}_2(\text{l})$, atomization of $\text{Br}_2(\text{g})$, electron attachment to Br(g), and formation of the solid MgBr_2 lattice from gaseous ions

$$\begin{aligned}\Delta_\text{f}H^\ominus(\text{MgBr}_2,\text{s}) = {} & \Delta_{\text{sub}}H^\ominus(\text{Mg},\text{s}) + \Delta_{\text{ion}}H^\ominus(\text{Mg},\text{g}) + \Delta_{\text{vap}}H^\ominus(\text{Br}_2,\text{l}) \\ & + \Delta_{\text{bond diss}}H^\ominus(\text{Br}_2,\text{g}) + 2\Delta_{\text{eg}}H^\ominus(\text{Br},\text{g}) - \Delta_\text{L}H^\ominus(\text{MgBr}_2,\text{s})\end{aligned}$$

So the lattice enthalpy is

$$\begin{aligned}\Delta_\text{L}H^\ominus(\text{MgBr}_2,\text{s}) = {} & \Delta_{\text{sub}}H^\ominus(\text{Mg},\text{s}) + \Delta_{\text{ion}}H^\ominus(\text{Mg},\text{g}) + \Delta_{\text{vap}}H^\ominus(\text{Br}_2,\text{l}) \\ & + \Delta_{\text{bond diss}}H^\ominus(\text{Br}_2,\text{g}) + 2\Delta_{\text{eg}}H^\ominus(\text{Br},\text{g}) - \Delta_\text{f}H^\ominus(\text{MgBr}_2,\text{s})\end{aligned}$$

$$\Delta_\text{L}H^\ominus(\text{MgBr}_2,\text{s}) = [148 + 2187 + 31 + 193 - 2(331) + 524]\text{ kJ mol}^{-1} = \boxed{2421\text{ kJ mol}^{-1}}$$

E19.26(b) Young's modulus: $E = \dfrac{\text{normal stress}}{\text{normal strain}}$ [9.13a] $= 215\ \text{GPa} = 215 \times 10^9\ \text{kg m}^{-1}\ \text{s}^{-2}$

We solve this relationship for the normal strain after calculating the normal stress from the data provided.

normal stress = force per unit area = F/A

normal strain = relative elongation = $\Delta L/L$

$$\Delta L/L = \frac{F/A}{E} = \frac{mg/A}{E} = \frac{mg}{AE} = \frac{mg}{\pi(d/2)^2 E}$$

$$= \frac{10.0\ \text{kg} \times (9.81\ \text{m s}^{-2})}{\pi(0.10 \times 10^{-3}\ \text{m}/2)^2 \times (215 \times 10^9\ \text{kg m}^{-1}\,\text{s}^{-2})}$$

$$= \boxed{0.058} \text{ or about 5.8\% elongation}$$

E19.27(b) Poisson's ratio: $\nu_\text{p} = \dfrac{\text{transverse strain}}{\text{normal strain}}$ [19.17] $= 0.41$

We note that the transverse strain is usually a contraction and that it is usually evenly distributed in both transverse directions. That is, if $(\Delta L/L)_z$ is the normal strain, then the transverse strains, $(\Delta L/L)_x$ and $(\Delta L/L)_y$, are equal. In this case of a 2.0% uniaxial stress:

$$\left(\frac{\Delta L}{L}\right)_z = +0.020, \quad \left(\frac{\Delta L}{L}\right)_x = \left(\frac{\Delta L}{L}\right)_y = -0.020 \times 0.41 = -0.0082 \text{ [a contraction of widths]}$$

Application of the stress to a 1 dm^3 cube of lead results in a volume equal to

$$(1 - 0.0082)^2 \times (1 + 0.020) \times 1\ \text{dm}^3 = 1.0033\ \text{dm}^3$$

The change in volume is $\boxed{3.3 \times 10^{-3}\ \text{dm}^3}$.

E19.28(b) p-type; the dopant, gallium, belongs to Group 13, whereas germanium belongs to Group 14.

E19.29(b) $E_\text{g} = h\nu_\text{min}$

$$\nu_\text{min} = \frac{h}{E_\text{g}} = \frac{6.626 \times 10^{-34}\ \text{J s}}{1.12\ \text{eV}}\left(\frac{1\ \text{eV}}{1.602 \times 10^{-19}\ \text{J}}\right) = 3.69 \times 10^{-15}\ \text{s}^{-1} = \boxed{3.69\ \text{fHz}}$$

E19.30(b) $\mu = g_\text{e}\{S(S+1)\}^{1/2}\mu_\text{B}$ [19.34, with S in place of s]

Therefore, since $\mu = 5.3\ \mu_\text{B}$ and $g_\text{e} \approx 2$,

$$S(S+1) = (\tfrac{1}{4}) \times (5.3)^2 = 7.02, \quad \text{implying that} \quad S = 2.20 = \tfrac{4.40}{2}$$

Since $S \approx \frac{4.4}{2}$, the Mn^{2+} ions have $\boxed{\text{four to five unpaired spins}}$.

E19.31(b) $\chi_\text{m} = \chi V_\text{m}$[19.28] $= \chi M/\rho = (-7.9 \times 10^{-7}) \times (84.15\ \text{g mol}^{-1})/(0.811\ \text{g cm}^{-3}) = \boxed{-8.2 \times 10^{-5}\ \text{cm}^3\ \text{mol}^{-1}}$

E19.32(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \,[19.35], \quad \text{so} \quad S(S+1) = \frac{3kT\chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$

Using $\chi_m = 5.03 \times 10^{-8}\ \text{m}^3\ \text{mol}^{-1}$ [Table 19.6], we find that

$$S(S+1) = \frac{3(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})}{(6.022 \times 10^{23}\ \text{mol}^{-1}) \times (2.0023)^2} \times \frac{(5.03 \times 10^{-8}\ \text{m}^3\ \text{mol}^{-1})}{(4\pi \times 10^{-7}\ \text{T}^2\ \text{J}^{-1}\ \text{m}^3) \times (9.274 \times 10^{-24}\ \text{J T}^{-1})^2}$$

$$= 2.38, \quad \text{so} \quad S = \frac{-1+\sqrt{1+4(2.84)}}{2} = 1.12$$

corresponding to $\boxed{2.24}$ effective unpaired spins. The theoretical number is $\boxed{2}$. The magnetic moments in a crystal are close together, and they interact rather strongly. The discrepancy is most likely due to an interaction among the magnetic moments.

E19.33(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \,[19.35]$$

Mn^{2+} has five unpaired spins, so $S = 2.5$ and

$$\chi_m = \frac{(6.022 \times 10^{23}\ \text{mol}^{-1}) \times (2.0023)^2 \times (4\pi \times 10^{-7}\ \text{T}^2\ \text{J}^{-1}\ \text{m}^3) \times (9.274 \times 10^{-24}\ \text{J T}^{-1})^2 \times (2.5) \times (2.5+1)}{3(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})}$$

$$= \boxed{1.85 \times 10^{-7}\ \text{m}^3\ \text{mol}^{-1}}$$

E19.34(b) The relationship between critical temperature and critical magnetic field is given by

$$\mathcal{H}_c(T) = \mathcal{H}_c(0)\left(1 - \frac{T^2}{T_c^2}\right) [19.36]$$

Solving for T gives the critical temperature for a given magnetic field:

$$T = T_c\left(1 - \frac{\mathcal{H}_c(T)}{\mathcal{H}_c(0)}\right)^{1/2} = (3.72\ \text{K}) \times \left(1 - \frac{15\ \text{kA m}^{-1}}{25\ \text{kA m}^{-1}}\right)^{1/2} = \boxed{2.4\ \text{K}}$$

Solutions to problems

Solutions to numerical problems

P19.2 The powder diffraction pattern shows a reflection from the (100) plane, so we may conclude that polonium has the $\boxed{\text{simple (primitive) cubic lattice}}$ because, as indicated in text Figure 9.23, the face-centred and body-centred cubic lattices do not exhibit this line. Furthermore, only the primitive cubic lattice shows a powder diffraction pattern in which the separation between the sixth and seventh lines is larger than between the fifth and sixth lines (see text Figure 19.23).

$$d_{100} = a\,[19.2] = \frac{\lambda}{2\sin\theta}\,[19.5]$$

$$a = \frac{154\ \text{pm}}{(2)\times(0.225)} = \boxed{342\ \text{pm}}$$

P19.4 $\lambda = 2a\sin\theta_{100}$ as $d_{100} = a$

Therefore, $a = \dfrac{\lambda}{2\sin\theta_{100}}$ and

$$\frac{a(\text{KCl})}{a(\text{NaCl})} = \frac{\sin\theta_{100}(\text{NaCl})}{\sin\theta_{100}(\text{KCl})} = \frac{\sin 6°0'}{\sin 5°23'} = 1.114$$

Therefore, $a(\text{KCl}) = (1.114)\times(564\ \text{pm}) = \boxed{628\ \text{pm}}$

The relative densities calculated from these unit cell dimensions are

$$\frac{\rho(\text{KCl})}{\rho(\text{NaCl})} = \left(\frac{M(\text{KCl})}{M(\text{NaCl})}\right)\times\left(\frac{a(\text{NaCl})}{a(\text{KCl})}\right)^3 = \left(\frac{74.55}{58.44}\right)\times\left(\frac{564\ \text{pm}}{628\ \text{pm}}\right)^3 = 0.924$$

Experimentally,

$$\frac{\rho(\text{KCl})}{\rho(\text{NaCl})} = \frac{1.99\ \text{g cm}^{-3}}{2.17\ \text{g cm}^{-3}} = 0.917$$

and the measurements $\boxed{\text{are broadly consistent}}$.

P19.6 As demonstrated in *Justification* 19.3 of the text, close-packed spheres fill 0.7404 of the total volume of the crystal. Therefore, 1 cm^3 of close-packed carbon atoms would contain

$$\frac{0.74040\ \text{cm}^3}{(\frac{4}{3}\pi r^3)} = 3.838\times10^{23}\ \text{atoms}$$

$$\left(r = \left(\frac{154.45}{2}\right)\text{pm} = 77.225\ \text{pm} = 77.225\times10^{-10}\ \text{cm}\right)$$

Hence, the close-packed density would be

$$\rho = \frac{\text{mass in 1 cm}^3}{1\ \text{cm}^3} = \frac{(3.838\times10^{23}\ \text{atom})\times(12.01\,m_u/\text{atom})\times(1.6605\times10^{-24}\ \text{g}\,m_u^{-1})}{1\ \text{cm}^3}$$

$$= \boxed{7.654\ \text{g cm}^{-3}}$$

The diamond structure is a very open structure that is dictated by the tetrahedral bonding of the carbon atoms. As a result, many atoms that would be touching each other in a normal fcc structure do not in diamond, for example the C atom in the centre of a face does not touch the C atoms at the corners of the face. See text Figure 19.41.

P19.8 As indicated in Exercise 19.7, the volume of a primitive monoclinic unit cell is

$$V = abc\sin\beta = (1.0427\ \text{nm})\times(0.8876\ \text{nm})\times(1.3777\ \text{nm})\times\sin(93.254°) = 1.2730\ \text{nm}^3$$

The mass per unit cell is

$$m = \rho V = (2.024\ \text{g cm}^{-3}) \times (1.2730\ \text{nm}^3) \times (10^{-7}\ \text{cm nm}^{-1})^3 = 2.577 \times 10^{-21}\ \text{g}$$

The monomer is $CuC_7H_{13}N_5O_8S$, so its molar mass is

$$M = [(63.546) + 7(12.011) + 13(1.008) + 5(14.007) + 8(15.999) + 32.066]\ \text{g mol}^{-1} = 390.82\ \text{g mol}^{-1}$$

The number of monomer units, then, is the mass of the unit cell divided by the mass of the monomer

$$N = \frac{mN_A}{M} = \frac{(2.577 \times 10^{-21}\ \text{g}) \times (6.022 \times 10^{23}\ \text{mol}^{-1})}{390.82\ \text{g mol}^{-1}} = 3.97 \quad \text{or} \quad \boxed{4}$$

P19.10 The length of an edge in the fcc lattice of these compounds is $a = 2(r_+ + r_-)$. Then,

(1) $a(\text{NaCl}) = 2(r_{\text{Na}^+} + r_{\text{Cl}^-}) = 562.8\ \text{pm}$

(2) $a(\text{KCl}) = 2(r_{\text{K}^+} + r_{\text{Cl}^-}) = 627.7\ \text{pm}$

(3) $a(\text{NaBr}) = 2(r_{\text{Na}^+} + r_{\text{Br}^-}) = 596.2\ \text{pm}$

(4) $a(\text{KBr}) = 2(r_{\text{K}^+} + r_{\text{Br}^-}) = 658.6\ \text{pm}$

If the ionic radii of all the ions are constant then

$(1) + (4) = (2) + (3)$

$(1) + (4) = (562.8 + 658.6)\ \text{pm} = 1221.4\ \text{pm}$

$(2) + (3) = (627.7 + 596.2)\ \text{pm} = 1223.9\ \text{pm}$

The difference is slight, $\boxed{\text{hence the data support}}$ the constancy of the radii of the ions.

P19.12 When a very narrow X-ray beam (with a spread of wavelengths) is directed on the centre of a genuine pearl, all the crystallites are irradiated parallel to a trigonal axis and the result is a Laue photograph with sixfold symmetry. In a cultured pearl the narrow beam will have an arbitrary orientation with respect to the crystallite axes (of the central core) and an unsymmetrical Laue photograph will result. (See J. Bijvoet *et al.*, *X-ray analysis of crystals* (London: Butterworth, 1951).)

P19.14 (a) When there is only one pair of identical atoms, the Wierl equation reduces to

$$I(\theta) = f^2 \frac{\sin sR}{sR}, \quad \text{where} \quad s = \frac{4\pi}{\lambda} \sin \frac{1}{2}\theta$$

Extrema occur at $sR = \dfrac{\sin sR}{\cos sR} = \tan sR$ and this equation may be solved either graphically or numerically to give the extrema values shown in the plot of Figure 19.6.

The angles of extrema are calculated using the Br_2 bond length of 228.3 pm, the equation $\theta = 2\sin^{-1}\left(\dfrac{sR\lambda}{4\pi R}\right)$, and sR extrema values shown in Figure 19.6.

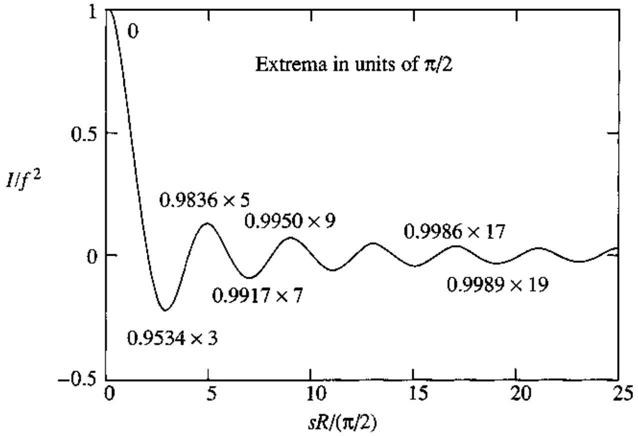


Figure 19.6

Neutron diffraction: $\theta_{\text{1st max}} = 0$

$$\theta_{\text{1st min}} = 2\sin^{-1}\left(\frac{(0.9534 \times 3\pi/2) \times (78\ \text{pm})}{4\pi(228.3\ \text{pm})}\right) = \boxed{14.0°}$$

$$\theta_{\text{2nd max}} = 2\sin^{-1}\left(\frac{(0.9836 \times 5\pi/2) \times (78\ \text{pm})}{4\pi(228.3\ \text{pm})}\right) = \boxed{24.2°}$$

Electron diffraction: $\theta_{\text{1st max}} = 0$

$$\theta_{\text{1st min}} = 2\sin^{-1}\left(\frac{(0.9534 \times 3\pi/2) \times (4.0\ \text{pm})}{4\pi(228.3\ \text{pm})}\right) = \boxed{0.72°}$$

$$\theta_{\text{2nd max}} = 2\sin^{-1}\left(\frac{(0.9836 \times 5\pi/2) \times (4\ \text{pm})}{4\pi(228.3\ \text{pm})}\right) = \boxed{1.23°}$$

(b) $$I = \sum_{i,j} f_i f_j \frac{\sin sR_{i,j}}{sR_{i,j}}, \quad s = \frac{4\pi}{\lambda}\sin\frac{1}{2}\theta$$

$$= 4f_{\text{C}}f_{\text{Cl}}\frac{\sin sR_{\text{CCl}}}{sR_{\text{CCl}}} + 6f_{\text{Cl}}^2\frac{\sin sR_{\text{ClCl}}}{sR_{\text{ClCl}}} \text{ [4 C – Cl pairs, 6 Cl – Cl pairs]}$$

$$= (4) \times (6) \times (17) \times (f^2) \times \left(\frac{\sin x}{x}\right) + (6) \times (17)^2 \times (f^2) \times \frac{\sin(\frac{8}{3})^{1/2}x}{(\frac{8}{3})^{1/2}x} \quad [x = sR_{\text{CCl}}]$$

$$\frac{I}{f^2} = (408) \times \frac{\sin x}{x} + (1062)\frac{\sin(\frac{8}{3})^{1/2}x}{x}$$

A plot of this function is shown in Figure 19.7.

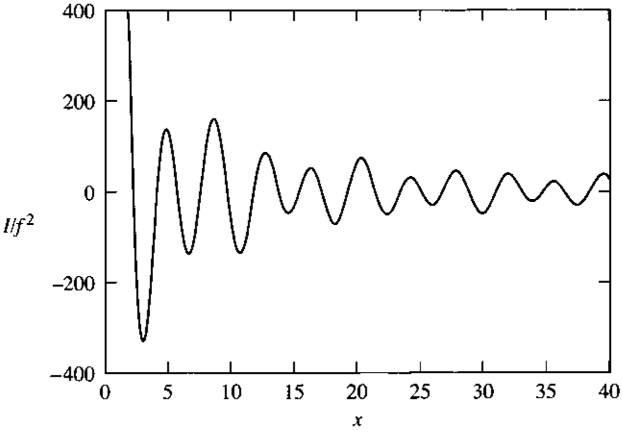


Figure 19.7

We find $x_{\max}$ and $x_{\min}$ from the graph, and $s_{\max}$ and $s_{\min}$ from the data. Then, since $x = sR_{\mathrm{CCl}}$, we can take the ratio x/s to find the bond length R_{CCl}. The calculation of s requires the wavelength of the electron beam.

$$\frac{p^2}{2m_e} = eV \quad \text{or} \quad p = (2m_e eV)^{1/2}$$

From the de Broglie relationship,

$$\lambda = \frac{h}{p} = \frac{h}{(2m_e eV)^{1/2}} = \frac{6.626 \times 10^{-34}\ \mathrm{J\ s}}{2 \times (9.109 \times 10^{-31}\ \mathrm{kg}) \times (1.609 \times 10^{-19}\ \mathrm{C}) \times (1.00 \times 10^{4}\ \mathrm{V})} = 12.2\ \mathrm{pm}$$

We draw up the following table:

θ(expt.)	Maxima			Minima			
	3°0′	5°22′	7°54′	1°46′	4°6′	6°40′	9°10′
s/pm^{-1}	0.0270	0.0482	0.0710	0.0159	0.0368	0.0599	0.0819
x(calc.)	4.77	8.52	12.6	2.89	6.52	10.6	14.5
(x/s)/pm	177	177	177	177	177	177	177

Hence, $\boxed{R_{\mathrm{CCl}} = 177\ \mathrm{pm}}$ and the experimental diffraction pattern is consistent with tetrahedral geometry.

P19.16 $G = G_0 e^{-E_g/2kT}$

$$\ln(G/\mathrm{S}) = \ln(G_0/\mathrm{S}) - \left(\frac{E_g}{2k}\right) \times \frac{1}{T}$$

Thus, the slope of a $\ln(G)$ against $1/T$ plot equals $-E_g/2k$. The data have minimal uncertainty so the slope can be calculated by the two-point difference method. Alternatively, a linear regression fit of $(1/T, \ln(G/\mathrm{S}))$ data points gives the slope:

$$slope = \frac{\Delta \ln(G/S)}{\Delta\left(\frac{1}{T}\right)} = \frac{\ln(0.0847) - \ln(2.86)}{\frac{1}{312\ \text{K}} - \frac{1}{420\ \text{K}}} = -4270\ \text{K}$$

$$E_g = -2k \times slope = -2 \times (1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (-4270\ \text{K}) = 1.18 \times 10^{-19}\ \text{J}$$

This is equivalent to 71.0 kJ mol^{-1} or $\boxed{0.736\ \text{eV}}$.

P19.18 If the unit cell volume does not change on substitution of Ca for Y, then the density of the superconductor and that of the Y-only compound will be proportional to their molar masses.

$$M_{\text{super}} = [2(200.59) + 2(137.327) + (1 - x) \times (88.906) + x(40.078) + 2(63.546) + 7.55(15.999)]\ \text{g mol}^{-1}$$

$$M_{\text{super}}/(\text{g mol}^{-1}) = 1012.6 - 48.828x$$

The molar mass of the Y-only compound is 1012.6 g mol^{-1}, and the ratio of their densities is

$$\frac{\rho_{\text{super}}}{\rho_{\text{Y-only}}} = \frac{1012.6 - 48.828x}{1012.6} = 1 - 0.04822x, \quad \text{so} \quad x = \frac{1}{0.04822}\left(1 - \frac{\rho_{\text{super}}}{\rho_{\text{Y-only}}}\right)$$

The density of the Y-only compound is its mass over its volume. The volume is

$$V_{\text{Y-only}} = a^2c = (0.38606\ \text{nm})^2 \times (2.8915\ \text{nm}) = 0.43096\ \text{nm}^3 = 0.43096 \times 10^{-21}\ \text{cm}^3$$

so the density

$$\rho_{\text{Y-only}} = \frac{2M}{N_A V} = \frac{2 \times (1012.6\ \text{g mol}^{-1})}{(6.022 \times 10^{23}\ \text{mol}^{-1}) \times (0.43096 \times 10^{-21}\ \text{cm}^3)} = 7.804\ \text{g cm}^{-3}$$

The extent of Ca substitution is

$$x = \frac{1}{0.04822}\left(1 - \frac{7.651}{7.804}\right) = \boxed{0.41}$$

COMMENT. The precision of this method depends strongly on just how constant the lattice volume really is.

Solutions to theoretical problems

P19.20 If the sides of the unit cell define the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, then its volume is $V = \boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}$ [given]. Introduce the orthogonal set of unit vectors $\hat{\boldsymbol{i}}, \hat{\boldsymbol{j}}, \hat{\boldsymbol{k}}$ so that

$$\boldsymbol{a} = a_x\hat{\boldsymbol{i}} + a_y\hat{\boldsymbol{j}} + a_z\hat{\boldsymbol{k}}$$
$$\boldsymbol{b} = b_x\hat{\boldsymbol{i}} + b_y\hat{\boldsymbol{j}} + b_z\hat{\boldsymbol{k}}$$
$$\boldsymbol{c} = c_x\hat{\boldsymbol{i}} + c_y\hat{\boldsymbol{j}} + c_z\hat{\boldsymbol{k}}$$

Then, $V = \boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c} = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$

Therefore,

$$V^2 = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

$$= \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} \begin{vmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{vmatrix} \quad \text{[interchange rows and columns, no change in value]}$$

$$= \begin{vmatrix} a_xa_x + a_ya_y + a_za_z & a_xb_x + a_yb_y + a_zb_z & a_xc_x + a_yc_y + a_zc_z \\ b_xa_x + b_ya_y + b_za_z & b_xb_x + b_yb_y + b_zb_z & b_xc_x + b_yc_y + b_zc_z \\ c_xa_x + c_ya_y + c_za_z & c_xb_x + c_yb_y + c_zb_z & c_xc_x + c_yc_y + c_zc_z \end{vmatrix}$$

$$= \begin{vmatrix} a^2 & \boldsymbol{a}\cdot\boldsymbol{b} & \boldsymbol{a}\cdot\boldsymbol{c} \\ \boldsymbol{b}\cdot\boldsymbol{a} & b^2 & \boldsymbol{b}\cdot\boldsymbol{c} \\ \boldsymbol{c}\cdot\boldsymbol{a} & \boldsymbol{c}\cdot\boldsymbol{b} & c^2 \end{vmatrix} = \begin{vmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{vmatrix}$$

$$= a^2b^2c^2(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)$$

Hence, $\boxed{V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}}$

Thus, for a monoclinic cell, for which $\alpha = \gamma = 90°$, $V = abc(1 - \cos^2\beta)^{1/2} = abc\sin\beta$

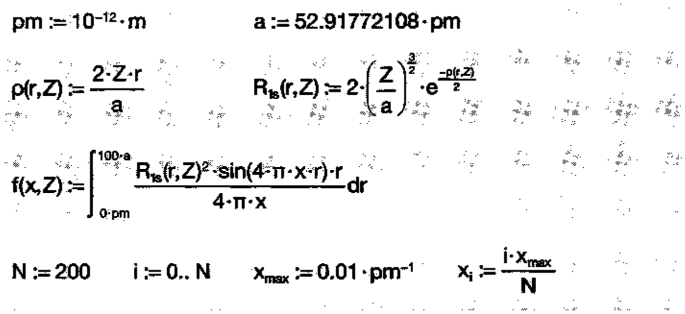
and for an orthorhombic cell, for which $\alpha = \beta = \gamma = 90°$, $V = abc$.

P19.22 The mathematical forms of the 1s and 2s radial wavefunctions are found in Table 9.1. For the one-electron hydrogen-like atom $4\pi\rho(r) = R(r)^2$ [9.18] and the scattering factor is given by

$$f(r,Z) = 4\pi\int_0^\infty \rho(r,Z)\frac{\sin(4\pi xr)}{4\pi xr}r^2\,\mathrm{d}r \text{ [9.6]}, \quad \text{where} \quad x = \frac{\sin\theta}{\lambda} = \int_0^\infty R(r,Z)^2\frac{\sin(4\pi xr)}{4\pi x}r\,\mathrm{d}r$$

The scattering factor equals one in the forward direction.

(a) The scattering factor of a 1s hydrogen-like orbital is calculated, and plotted, in the following Mathcad worksheet. An increase in the atomic number effectively moves the scattering factor away from the forward direction.

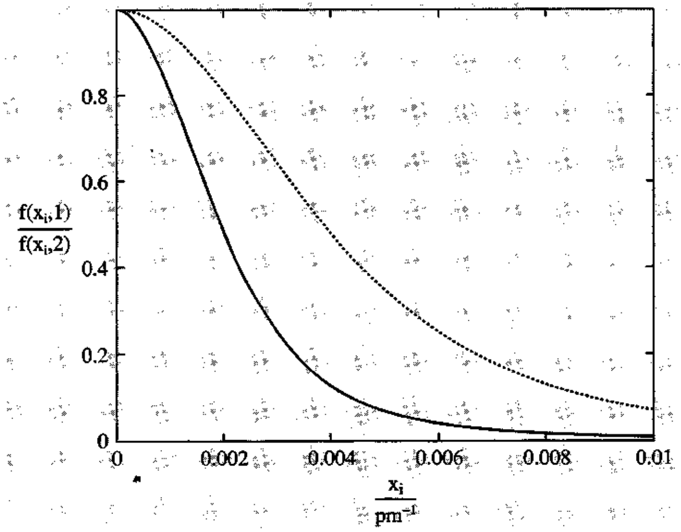


$\mathrm{pm} := 10^{-12}\cdot\mathrm{m}$ $\quad$ $a := 52.91772108\cdot\mathrm{pm}$

$\rho(r,Z) := \dfrac{2\cdot Z\cdot r}{a}$ $\quad$ $R_{1s}(r,Z) := 2\cdot\left(\dfrac{Z}{a}\right)^{\frac{3}{2}}\cdot e^{\frac{-\rho(r,Z)}{2}}$

$$f(x,Z) := \int_{0\cdot\mathrm{pm}}^{100\cdot a}\frac{R_{1s}(r,Z)^2\cdot\sin(4\cdot\pi\cdot x\cdot r)\cdot r}{4\cdot\pi\cdot x}\,\mathrm{d}r$$

$N := 200$ $\quad$ $i := 0..N$ $\quad$ $x_{max} := 0.01\cdot\mathrm{pm}^{-1}$ $\quad$ $x_i := \dfrac{i\cdot x_{max}}{N}$

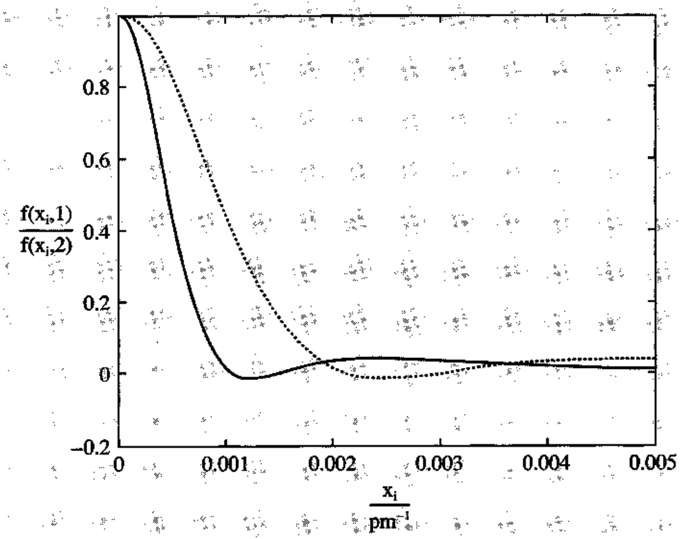


(b) The scattering factor of a 2s hydrogen-like orbital is calculated, and plotted, in the following Mathcad worksheet. An increase in the principal quantum number n moves the scattering factor towards the forward direction, while an increase in the atomic number effectively moves the scattering factor away from the forward direction.

$$\rho(r,Z) := \frac{Z\cdot r}{a} \qquad R_{2s}(r,Z) := 8^{\frac{-1}{2}}\cdot\left(\frac{Z}{a}\right)^{\frac{3}{2}}\cdot(2-\rho(r,Z))\cdot e^{\frac{-\rho(r,Z)}{2}}$$

$$f(x,Z) := \int_{0\cdot pm}^{100\cdot a} \frac{R_{2s}(r,Z)^2\cdot\sin(4\cdot\pi\cdot x\cdot r)\cdot r}{4\cdot\pi\cdot x}\,dr$$

$$N := 200 \qquad i := 0..N \qquad x_{max} := 0.005\cdot pm^{-1} \qquad x_i := \frac{i\cdot x_{max}}{N}$$



P19.24 Close-packed rods of length L and elliptical cross-section with semi-major axis a and semi-minor axis b have a rod volume of πabL. The parallelepiped unit cell is shown in Figure 19.8(a) in a cross-section of the packed rods. Examination of the figure reveals that each unit cell contains one rod. Thus, the packing fraction f is given by

$$f=\frac{\pi abL}{LA_p}=\frac{\pi ab}{A_p},\quad \text{where } A_p \text{ is the cross-section area of the unit cell.}$$

Figure 19.8(b) defines the parameters needed for the determination of A_p. Examination of the centre positions of a pair of stacked ellipses reveals that they have the relative coordinates (0,0) and (0,2b). The adjacent ellipse column is centred b higher and, consequently, the vertical contact point between the adjacent ellipses is necessarily at $b/2$. The horizontal component of the contact point, x, is calculated with the formula for an ellipse using $y=b/2$.

$$\left(\frac{x}{a}\right)^2+\left(\frac{y}{b}\right)^2=1$$

$$\left(\frac{x}{a}\right)^2+\left(\frac{b/2}{b}\right)^2=1 \quad \text{or} \quad x=\tfrac{1}{2}\sqrt{3}a$$

The parallelepiped area has a base of $2b$ and its height h is

$$h=2x=\sqrt{3}a$$

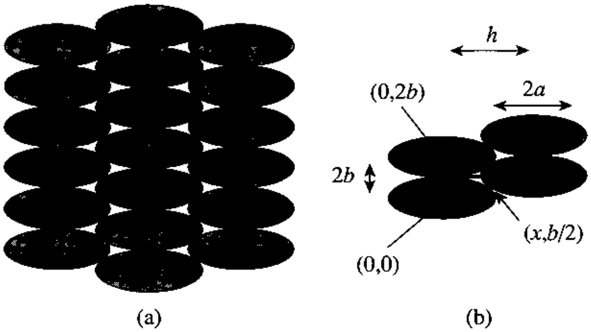
Thus,

$$A_p=2bh=2\sqrt{3}ab$$

and

$$f=\frac{\pi ab}{2\sqrt{3}ab}=\frac{\pi}{2\sqrt{3}}=\boxed{0.907}$$

The above formula for the packing fraction shows that it is independent of the ellipse eccentricity.



(a) (b)

Figure 19.8

P19.26 $$F_{hkl}=\sum_i f_i e^{2\pi i(hx_i+ky_i+lz_i)}\ [19.7]$$

For each A atom use $\frac{1}{8}f_A$ (each A atom shared by eight cells) but use f_B for the central atom (since it contributes solely to the cell).

$$\begin{aligned}F_{hkl} &= \tfrac{1}{8}f_{\mathrm{A}}\{1+\mathrm{e}^{2\pi \mathrm{i}h}+\mathrm{e}^{2\pi \mathrm{i}k}+\mathrm{e}^{2\pi \mathrm{i}l}+\mathrm{e}^{2\pi \mathrm{i}(h+k)}+\mathrm{e}^{2\pi \mathrm{i}(h+l)}+\mathrm{e}^{2\pi \mathrm{i}(k+l)}+\mathrm{e}^{2\pi \mathrm{i}(h+k+l)}\}+f_{\mathrm{B}}\mathrm{e}^{\pi \mathrm{i}(h+k+l)}\\ &= f_{\mathrm{A}}+(-1)^{(h+k+l)}f_{\mathrm{B}} \quad [h, k, l \text{ are all integers, } \mathrm{e}^{\mathrm{i}\pi}=-1]\end{aligned}$$

(a) $f_{\mathrm{A}}=f, \quad f_{\mathrm{B}}=0; \quad F_{hkl}=f$ $\boxed{\text{no systematic absences}}$

(b) $f_{\mathrm{B}}=\tfrac{1}{2}f_{\mathrm{A}}; \quad F_{hkl}=f_{\mathrm{A}}[1+\tfrac{1}{2}(-1)^{(h+k+l)}]$

Therefore, when $h+k+l$ is odd, $F_{hkl}=f_{\mathrm{A}}(1-\tfrac{1}{2})=\tfrac{1}{2}f_{\mathrm{A}}$, and when $h+k+l$ is even, $F_{hkl}=\tfrac{3}{2}f_{\mathrm{A}}$.

That is, there is an $\boxed{\text{alternation of intensity}}$ ($I \propto F^2$) according to $\boxed{\text{whether } h+k+l \text{ is odd or even}}$.

(c) $f_{\mathrm{A}}=f_{\mathrm{B}}=f; \quad F_{hkl}=f\{1+(-1)^{h+k+l}\}=0$ if $h+k+l$ is odd.

Thus, $\boxed{\text{all } h+k+l \text{ odd lines are missing}}$.

P19.28 According to eqn 19.18:

$$G=\frac{E}{2(1+\nu_{\mathrm{P}})} \quad \text{and} \quad K=\frac{E}{3(1-2\nu_{\mathrm{P}})}$$

Substituting the Lamé-constant expressions for E and ν_{P} into the right-hand side of these relationships yields:

$$G=\frac{\dfrac{\mu(3\lambda+2\mu)}{\lambda+\mu}}{2\left(1+\dfrac{\lambda}{2(\lambda+\mu)}\right)} \quad \text{and} \quad K=\frac{\dfrac{\mu(3\lambda+2\mu)}{\lambda+\mu}}{3\left(1-\dfrac{\lambda}{\lambda+\mu}\right)}.$$

Expanding leads to:

$$G=\frac{\dfrac{\mu(3\lambda+2\mu)}{\lambda+\mu}}{2\left(\dfrac{2\lambda+2\mu+\lambda}{2(\lambda+\mu)}\right)}=\frac{\mu(3\lambda+2\mu)}{3\lambda+2\mu}=\boxed{\mu}$$

$$\text{and} \quad K=\frac{\dfrac{\mu(3\lambda+2\mu)}{\lambda+\mu}}{3\left(\dfrac{\lambda+\mu-\lambda}{(\lambda+\mu)}\right)}=\frac{\mu(3\lambda+2\mu)}{3\mu}=\boxed{\frac{3\lambda+2\mu}{3}},$$

as the problem asks us to prove.

P19.30 Permitted states at the low-energy edge of the band must have a relatively long characteristic wavelength, while the permitted states at the high-energy edge of the band must have a relatively short characteristic wavelength. There are few wavefunctions that have these characteristics, so the density of states is lowest at the edges. This is analogous to the MO picture that shows a few bonding MOs that lack nodes and few antibonding MOs that have the maximum number of nodes.

Another insightful view is provided by consideration of the spatially periodic potential that the electron experiences within a crystal. The periodicity demands that the electron wavefunction be a periodic function of the position vector $\vec{r}$. We can approximate it with a Bloch wave, $\psi \propto e^{i\vec{k}\cdot\vec{r}}$, where $\vec{k} = k_x\hat{i} + k_y\hat{j} + k_z\hat{k}$ is called the wavenumber vector. This is a bold, 'free' electron approximation and in the spirit of searching for a conceptual explanation, not an accurate solution, suppose that the wavefunction satisfies a Hamiltonian in which the potential can be neglected: $\hat{H} = -(\hbar^2/2m)\nabla^2$. The eigenvalues of the Bloch wave are: $E = \hbar^2|\vec{k}|^2/2m$. The Bloch wave is periodic when the components of the wavenumber vector are multiples of a basic repeating unit. Writing the repeating unit as $2\pi/L$, where L is a length that depends on the structure of the unit cell, we find $k_x = 2n_x\pi/L$, where $n_x = 0, \pm1, \pm2, \ldots$. Similar equations can be written for k_y and k_z and with substitution the eigenvalues become $E = (1/2m)(2\pi\hbar/L)^2(n_x^2 + n_y^2 + n_z^2)$. This equation suggests that the density of states for energy level E can be visually evaluated by looking at a plot of permitted n_x, n_y, n_z values, as shown in Figure 19.9. The number of n_x, n_y, n_z values within a thin, spherical shell around the origin equals the density of states that have energy E. Three shells, labelled 1, 2, and 3, are shown in the graph. All have the same width but their energies increase with their distance from the origin. It is obvious that the low-energy shell 1 has a much lower density of states than the intermediate energy shell 2. The sphere of shell 3 has been cut into the shape determined by the periodic potential pattern of the crystal and, because of this phenomena, it also has a lower density of states than the intermediate energy shell 2. The general concept is that the low-energy and high-energy edges of a band have lower density of states than that of the band centre.

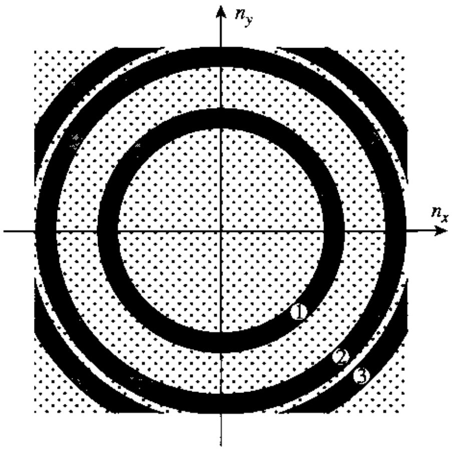


Figure 19.9

P19.32 (a) $\hat{H}\psi_{+\text{or}-} = \tilde{\nu}_{+\text{or}-}\psi_{+\text{or}-}$ and $(\hat{H} - \tilde{\nu}_{+\text{or}-})\psi_{+\text{or}-} = 0$

$$\begin{pmatrix} \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-} & \beta \\ \beta & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-} \end{pmatrix}\psi_{+\text{or}-} = 0, \quad \text{where} \quad \beta = \frac{\mu_{\text{mon}}^2}{4\pi\varepsilon_0 hcr^3}(1 - 3\cos^2\theta)$$

$$\begin{pmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{pmatrix}\psi_{+\text{or}-} = 0, \quad \text{where} \quad x_{+\text{or}-} = (\tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-})/\beta$$

$$\begin{vmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{vmatrix} = x_{+\text{or}-}^2 - 1 = 0$$

$x_{+\text{or}-} = (\tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+\text{or}-})/\beta = \pm 1$ and $\tilde{\nu}_{+\text{or}-} = \tilde{\nu}_{\text{mon}} \pm \beta$

$\tilde{\nu}_{+} = \tilde{\nu}_{\text{mon}} - \beta$ and $\tilde{\nu}_{-} = \tilde{\nu}_{\text{mon}} + \beta$

$\tilde{\nu}_{+}$ and $\tilde{\nu}_{-}$ are poltted below (Figure 19.10) as a function of θ using $\mu_{\text{mon}} = 4.00$ D, $\tilde{\nu}_{\text{mon}} = 25\,000\ \text{cm}^{-1}$, and $r = 0.5$ nm.

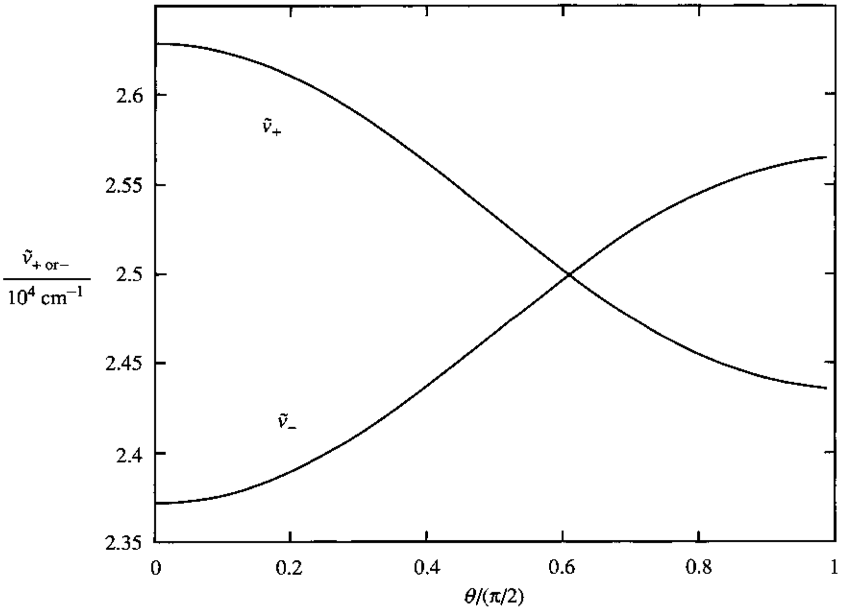


Figure 19.10

The ratio of μ_{+}^2/μ_{-}^2 (and the relative intensities of the dimer transitions) does not depend on β or θ because $\mu_{+} = 0$. To see this, we use the coefficients of the normalized wavefunctions for ψ_{+} and ψ_{-} and the overlap integral $S = \langle\psi_1|\psi_2\rangle$.

$$\begin{pmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{pmatrix}\begin{pmatrix} c_{+\text{or}-,1} \\ c_{+\text{or}-,2} \end{pmatrix} = 0, \quad \text{where} \quad x_{+\text{or}-} = \pm 1$$

$$x_{+\text{or}-}c_{+\text{or}-,1} + c_{+\text{or}-,2} = 0$$

$$c_{+\text{or}-,2} = -x_{+\text{or}-}c_{+\text{or}-,1} \quad \text{(i)}$$

The coefficients must also satisfy the normalization condition.

$$\begin{aligned}\langle\psi_{+\text{or}-}|\psi_{+\text{or}-}\rangle &= \langle c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2 | c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2\rangle \\ &= c_{+\text{or}-,1}^2 + c_{+\text{or}-,2}^2 + 2c_{+\text{or}-,1}c_{+\text{or}-,2}S \\ &= c_{+\text{or}-,1}^2 + c_{+\text{or}-,1}^2 - 2x_{+\text{or}-}c_{+\text{or}-,1}^2 S = 1 \quad \text{(ii)}\end{aligned}$$

Thus,

$$c_{+,1} = \frac{1}{\{2(1-S)\}^{1/2}} \qquad c_{+,2} = -c_{+,1}$$

and

$$c_{-,1} = \frac{1}{\{2(1+S)\}^{1/2}} \qquad c_{-,2} = c_{-,1}$$

$$\frac{\mu_+^2}{\mu_-^2} = \left(\frac{\mu_+}{\mu_-}\right)^2 = \left(\frac{(c_{+,1}+c_{+,2})\mu_{\text{mon}}}{(c_{-,1}+c_{-,2})\mu_{\text{mon}}}\right)^2 \text{[see Problem 19.31]} = \left(\frac{c_{+,1}-c_{+,1}}{c_{-,1}+c_{-,1}}\right)^2 = 0$$

(b) The secular determinant for N monomers has the dimension $N \times N$.

$$\begin{vmatrix} \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & V & 0 & \cdots \\ V & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & V & \cdots \\ 0 & V & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{vmatrix} = 0$$

$$\tilde{\nu}_{\text{dimer}} = \tilde{\nu}_{\text{mon}} + 2V\cos\left(\frac{k\pi}{N+1}\right) \quad k = 1, 2, 3, \ldots, N \text{ [19.21]}$$

$$V = \beta(0) = \frac{\mu_{\text{mon}}^2}{4\pi\varepsilon_0 hcr^3}(1 - 3\cos^2 0) = \frac{-\mu_{\text{mon}}^2}{2\pi\varepsilon_0 hcr^3}$$

The following plot, Figure 19.11, shows the dimer transitions for $\theta = 0$ and $N = 15$. The shape of the transition distribution changes slightly with N and transition energies are symmetrically distributed around the monomer transition. The lowest-energy transition changes only slightly with N giving a value that goes to

$$25\,000\ \text{cm}^{-1} + 2V = 25\,000\ \text{cm}^{-1} + 2 \times (-1289\ \text{cm}^{-1}) = 22\,422\ \text{cm}^{-1} \text{ as } N \to \infty$$

Since the model considers only nearest-neighbour interactions, the transition dipole moment of the lowest energy transition does not depend on the size of the chain.

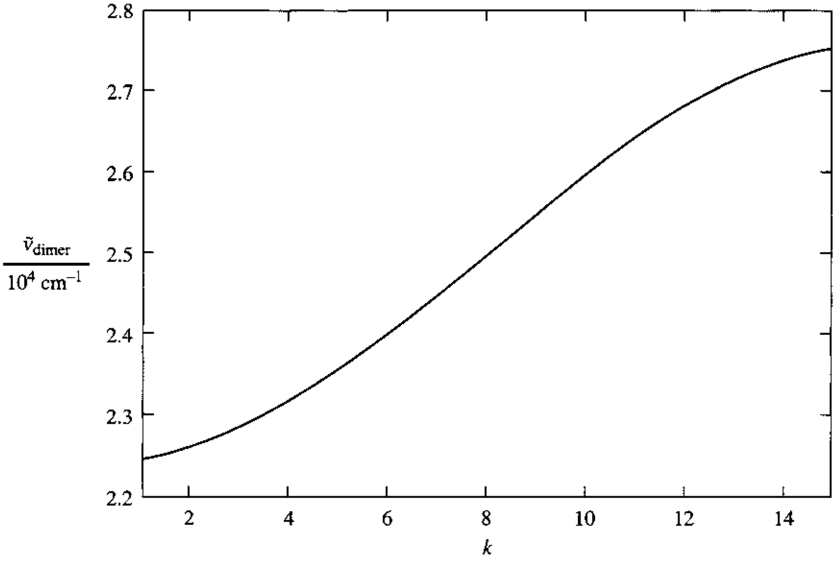


Figure 19.11

P19.34

$$\xi = \frac{-e^2}{6m_e}\langle r^2\rangle$$

$$\langle r^2\rangle = \int_0^\infty r^2\psi^2\,d\tau \quad \text{with} \quad \psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0} = 4\pi\int_0^\infty r^4\psi^2\,dr \quad [d\tau = 4\pi r^2\,dr]$$

$$= \frac{4}{a_0^3}\int_0^\infty r^4 e^{-2r/a_0}\,dr = 3a_0^2 \quad \left[\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}\right]$$

Therefore, $\boxed{\xi = \dfrac{-e^2a_0^2}{2m_e}}$

Then, since $\chi_m = N_A\mu_0\xi$ [19.30 with $m = 0$]

$$\chi_m = \boxed{\frac{-N_A\mu_0 e^2 a_0^2}{2m_e}}$$

P19.36 Only two electronic levels are accessible to nitric oxide at low temperature. The ground state is a doubly degenerate $^2\Pi_{1/2}$ state, while the excited state is a doubly degenerate $^2\Pi_{3/2}$ state that is 121.1 cm^{-1} above the ground state. These states originate from spin–orbital coupling of angular momentum. Let $\varepsilon = hc\tilde{\nu}$ be the energy separation between these levels, then the probabilities that a molecule is in one ($p_{1/2}$) or the other ($p_{3/2}$) level are given by eqn 15.14 as (these equations are derived from the Boltzmann distribution in the note below)

$$p_{1/2} = \frac{1}{1+e^{-\varepsilon/kT}} \quad \text{and} \quad p_{3/2} = \frac{e^{-\varepsilon/kT}}{1+e^{-\varepsilon/kT}} = \frac{1}{1+e^{\varepsilon/kT}} \; [15.14]$$

Since the ground state of nitric oxide exhibits no paramagnetism, only $p_{3/2}N_A$ molecules contribute to the observed magnetic moment of a mole of nitric oxide molecules. Consequently, eqn 19.35 for the molar paramagnetic susceptibility must be modified with the inclusion of a factor $p_{3/2}$:

$$\chi_m = \frac{p_{3/2}N_A g_e^2\mu_0\mu_B^2 S(S+1)}{3kT} \; [19.35]$$

Substitution of $S(S+1) = (\mu/g_e\mu_B)^2$ [19.34 with S substituted for s] where μ is the magnetic moment into the above expression gives

$$\chi_m = \frac{p_{3/2}N_A\mu_0\mu_B^2(\mu/\mu_B)^2}{3kT}$$

$$= \frac{N_A\mu_0\mu_B^2(\mu/\mu_B)^2}{3kT\times(1+e^{\varepsilon/kT})}, \quad \text{where} \quad \varepsilon/k = hc\tilde{\nu}/k = hc\times(121.1\text{ cm}^{-1})/k = 174.2\text{ K}$$

Thus, with $\mu/\mu_B = 2$

$$\chi_m = \frac{6.286\times10^{-6}\text{ m}^3\text{ mol}^{-1}}{(T/\text{K})\times(1+e^{174.2/(T/\text{K})})}$$

This relationship gives the molar paramagnetic susceptibility of NO as a function of temperature. For example, χ_m at 90 K is

$$\chi_m = \frac{6.286\times10^{-6}\text{ m}^3\text{ mol}^{-1}}{90\times(1+e^{174.2/(90)})} = 8.81\times10^{-9}\text{ m}^3\text{ mol}^{-1}$$

The mass paramagnetic susceptibility is

$$\chi_{\text{mass}} = \chi_{\text{m}}/M = (8.81\times10^{-9}\text{ m}^3\text{ mol}^{-1})/(0.03001\text{ kg mol}^{-1}) = 2.94\times10^{-7}\text{ m}^3\text{ kg}^{-1}$$

Wishing to compare this with the value found in the older literature, we must convert the SI unit of susceptibility to the cgs (or emu) unit by dividing the SI unit by 4π, converting the m^3 to cm^3, and converting kg to g:

$$\chi_{\text{mass}}\text{ in cgs} = (2.94\times10^{-4}\text{ cm}^3\text{ g}^{-1})/4\pi = 23.4\times10^{-6}\text{ cm}^3\text{ g}^{-1}$$

This is in reasonable agreement with the accepted value of 19.8×10^{-6} cgs for the mass susceptibility of NO(s) at 90 K. Figure 19.12 is a plot of the molar paramagnetic susceptibility, as modelled in this problem, against temperature below the normal fusion point (110 K) of nitric oxide. The curve is remarkably different from the $\chi_{\text{m}}(T)$ behaviour of most paramagnetic substances. Paramagnetism is normally a property of the ground electronic state and, consequently, there is an inverse relationship between χ_{m} and T [19.33] so that χ_{m} decreases with increasing T. Effective angular momenta of individual molecules align in a magnetic field at low temperature and become disoriented by thermal agitation as the temperature is increased. In the case of NO(s) it is the excited state that is paramagnetic so, when all molecules are in the ground state at absolute zero, $\chi_{\text{m}} = 0$. As T is increased from absolute zero, molecules are thermally promoted to the excited state and the observed paramagnetism increases, as shown in Figure 19.12.

COMMENT. The explanation of the magnetic properties of NO is more complicated and subtle than indicated by the solution here. In fact, the full solution for this case was one of the important triumphs of the quantum theory of magnetism, which was developed in about 1930. See J. H. van Vleck, *The theory of electric and magnetic susceptibilities*. Oxford University Press (1932).

Note: The Boltzmann distribution indicates that the probability that a molecule is in the ground-state energy level is given by $p_0 \propto g_0$, where g_0 is the degeneracy of the ground state, while the probability that the molecule is in energy level 1, that is ε above the ground state, is given by $p_1 \propto g_1 e^{-\varepsilon/kT}$. For a two-level system the constant of proportionality is provided by the normalization condition that $p_0 + p_1 = 1$. Thus, the constant of proportionality is $1/(g_0 + g_1 e^{-\varepsilon/kT})$ and the probabilities are

$$p_0 = g_0/(g_0 + g_1 e^{-\varepsilon/kT}) \quad \text{and} \quad p_1 = g_1 e^{-\varepsilon/kT}/(g_0 + g_1 e^{-\varepsilon/kT})$$

In the special case for which $g_0 = g_1$ the probabilities simplify to those given at the top.

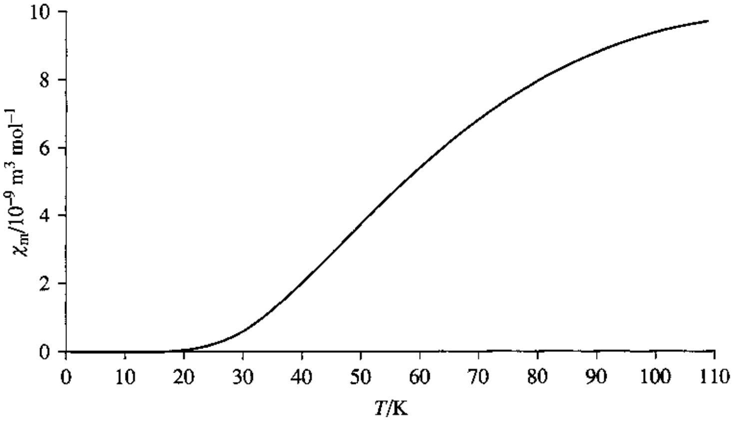
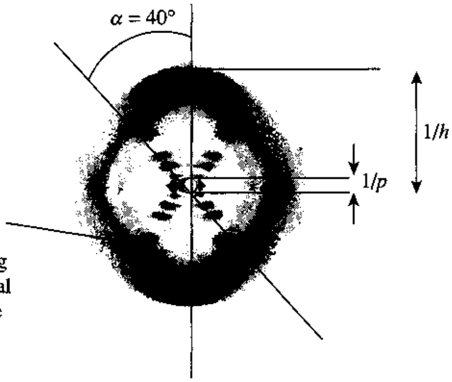


Figure 19.12

Solutions to applications: biochemistry and nanoscience

P19.38 The X-ray diffraction pattern of fibrous B-DNA (Figure 19.42 of the textbook) is discussed in *Impact on Biochemistry* 19.1: X-ray crystallography of biological macromolecules. Figures 19.43 and 19.44 of the text provide definitions of the helical tilt angle α and the base-layer spacing h. The helical pitch p is the vertical rise per turn of the helix. The characteristic X-shape of the diffraction pattern is that of a helix with incident radiation (Cu K_α 0.1542 nm) perpendicular to the cylindrical axis. An angle $\theta = 2.6°$ between the line of the incident radiation and the line from sample to the first spot on the X gives $p = \lambda/\sin\theta = 0.1542\text{ nm}/\sin(2.6°) = 3.4\text{ nm}$. Ten spots (counting two 'missing fourth' spots) along the X diagonal indicate that there are 10 base-planes per turn of the helix, with each accounting for a turn of 40°. The very large spot is at a distance $(1/h)$ that is 10 times the distance $1/p$ shown in Figure 19.13. Consequently, $h = 0.34$ nm. The missing fourth spots on the X diagonals indicate two coaxial sugar-phosphate backbones that are separated by $3p/8$ along the axis. The periodic h spacing of the large, very electron-dense phosphorous atoms causes the $1/h$ spots to be very intense. The fact that the fibrous X-ray sample was saturated with water suggests that the phosphates are to the outside.



Fourth spot in each direction is missing. Counting the missing spots, there are a total of 10 spots along the diagonal.

Figure 19.13

Figure 19.14 shows the two-dimensional zig-zag projection of the helical sugar-phosphate backbone onto a plane along the central axis. It serves to define the projection length l, perpendicular distance d between backbone planes, and the helix radius r. Examination of the right-hand triangle that shows the definition of α yields:

$$\tan(\alpha) = \frac{p}{4r} \quad \text{or} \quad r = \frac{p}{4\tan(\alpha)} = \frac{3.4\text{ nm}}{4\tan(40°)} = 1.0\text{ nm}$$

Examination of the right triangle containing the angle α also shows that $l\sin(\alpha) = p/2$, while the right triangle containing the angle 2α shows that $l\sin(2\alpha) = d$. Dividing these two equations yields:

$$\frac{\sin(2\alpha)}{\sin(\alpha)} = \frac{2d}{p} \quad \text{or} \quad \frac{2\sin(\alpha)\cos(\alpha)}{\sin(\alpha)} = \frac{2d}{p} \quad \text{or} \quad \cos(\alpha) = \frac{d}{p}$$

$$d = p\cos(\alpha) = (3.4\text{ nm})\cos(40°) = 2.6\text{ nm}$$

Finishing,

$$l = \frac{p}{2\sin(\alpha)} = \frac{3.4\,\text{nm}}{2\sin(40°)} = 2.6\,\text{nm}$$

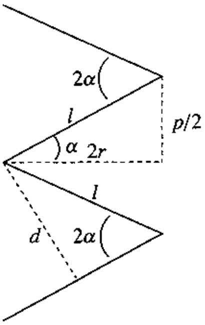
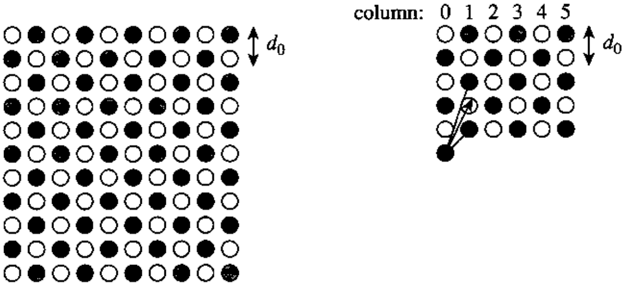


Figure 19.14

P19.40 Figure 19.15(a) shows a dark univalent probe cation in a vacancy within a two-dimensional square ionic lattice of grey univalent cations and white univalent anions. Let $d_0 = 200$ pm be the distance between nearest neighbours and let V_0 be the absolute value of the Coulombic interaction between nearest neighbours.

$$V_0 = \frac{e^2}{4\pi\varepsilon_0 d_0} = \frac{(1.602\times10^{-19}\,\text{C})^2}{(1.113\times10^{-10}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})\times(200\times10^{-12}\,\text{m})} = 1.153\times10^{-18}\,\text{J}$$

The symmetry of the lattice around the probe cation consists of four regions like that of Figure 19.15(b), so we calculate the total Coulombic interaction of the probe within the lattice quadrant of Figure 19.15(b) and multiply by 4. The calculation is pursued one column at a time and the column interactions are summed.



(a) (b)

Figure 19.15

Probe-to-column 0 interaction:

$$V_{\text{column }0} = -V_0 \times \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5}\cdots\right) = -V_0 \ln 2 = V_0 \sum_{n=1}^{\infty} \frac{(-1)^{n+0}}{(n^2+0^2)^{1/2}} \text{ (useful form)}$$

Probe-to-column 1 interaction using the Pythagorean theorem for the probe–ion distance:

$$V_{\text{column 1}} = V_0 \times \left(\frac{1}{2^{1/2}} - \frac{1}{5^{1/2}} + \frac{1}{10^{1/2}} - \frac{1}{17^{1/2}} \cdots \right) = V_0 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(n^2+1^2)^{1/2}}$$

Similarly, the probe-to-column m interaction, using the Pythagorean theorem for the probe–ion distance, is

$$V_{\text{column } m} = V_0 \sum_{n=1}^{\infty} \frac{(-1)^{n+m}}{(n^2+m^2)^{1/2}} \text{ for } 0 \le m < \infty \text{ (the sum is performed with a calculator or software)}$$

The total interaction for the region shown in Figure 19.15(b) is the sum of the above expression over all columns

$$\begin{aligned} V_{\text{Fig 19.15(b)}} &= V_0 \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \frac{(-1)^{n+m}}{(n^2+m^2)^{1/2}} \\ &= -0.4038V_0 = (-0.4038) \times (1.153 \times 10^{-18}\ \text{J}) \\ &= -4.656 \times 10^{-19}\ \text{J} \end{aligned}$$

The total Coulombic interaction of the probe cation with the lattice is

$$V_{\text{total}} = 4V_{\text{Fig 19.15(b)}} = 4(-4.656 \times 10^{-19}\ \text{J}) = \boxed{-1.862 \times 10^{-18}\ \text{J}}$$

where the negative value indicates a net attraction.

COMMENT. Suppose that you interpret the problem to involve placement of the probe cation at the foot of the two-dimensional step shown in Figure 19.16, you calculate the probe potential with

$$\begin{aligned} V_{\text{total}} &= 3V_{\text{Fig 19.15(b)}} - V_{\text{column 0}} \\ &= 3 \times (-0.4038V_0) - (-V_0 \ln 2) \\ &= -0.5183V_0 \\ &= (-0.5183) \times (1.153 \times 10^{-18}\ \text{J}) = \boxed{-5.975 \times 10^{-19}\ \text{J}} \end{aligned}$$

Once again, the negative value indicates a net attraction.

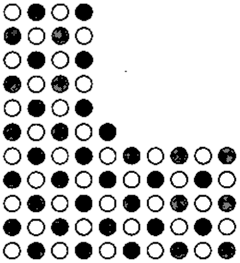
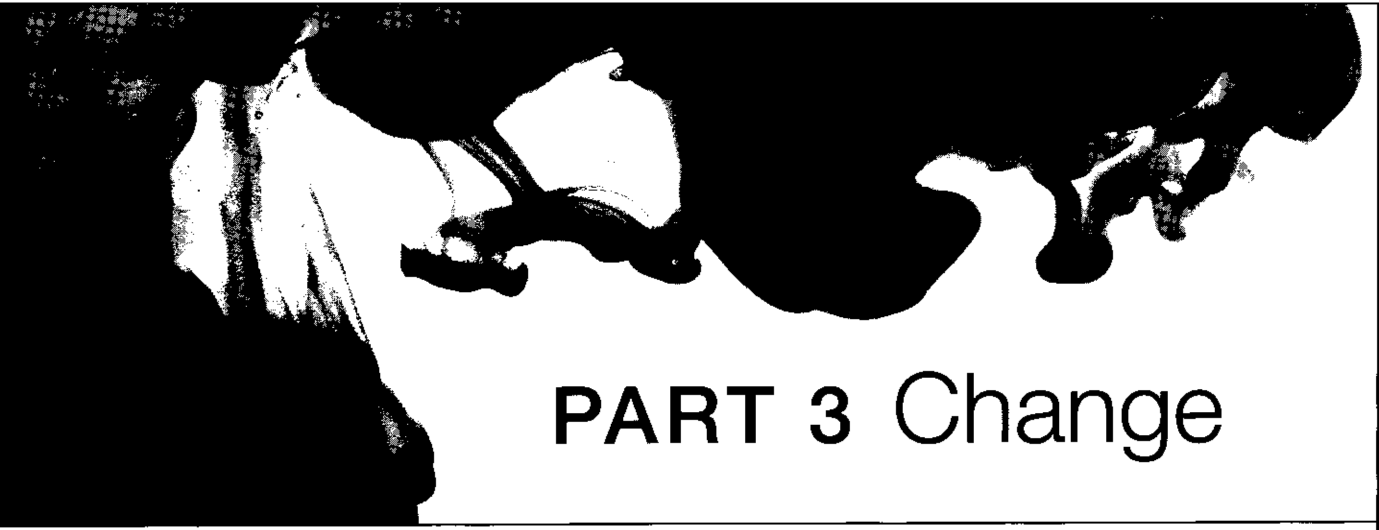


Figure 19.16



PART 3 Change

20

Molecules in motion

Answers to discussion questions

D20.2 Gases are very dilute systems and on average the molecules are very far apart from each other except when they collide, so what little resistance there is to flow in a gaseous fluid is almost entirely due to the collisions between molecules. The frequency of collisions increases with increasing temperature (see eqns 20.10, 20.9, and 20.7), hence the viscosity of gases increases with temperature. In liquids, on the other hand, the molecules are very close to each other, which results in there being strong forces of attraction between them that resist their movement relative to each other. However, as the temperature increases, more and more molecules are likely to have sufficient kinetic energy to overcome the forces of attraction, resulting in decreased viscosity.

D20.4 The **thermodynamic force** $\mathcal{F}$ is defined in eqn 20.43.

$$\mathcal{F} = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T} \quad [20.43]$$

This expression is a summary of the second thermodynamic law that molecules move in the direction that minimizes the chemical potential of the molecules when p and T are local constants. $\mathcal{F}$ is not one of the 'real' forces such as gravity or electromagnetism; it is the negative gradient of the chemical potential, which has a balance of terms involving enthalpy and entropy:

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} = \left(\frac{\partial}{\partial n_J}\right)_{p,T,n'} (H - TS)$$

Thus, the thermodynamic force moves molecules so as to minimize the enthalpy, to which molecular interactions provide a great contribution, while simultaneously attempting to maximize entropy. Often, one or the other of these tendencies predominate. For an ideal solution the gradient of the molar enthalpy is zero, so the force represents the spontaneous tendency for molecules to disperse so that entropy is maximized.

D20.6 Inelastic neutron-scattering measurements of scattering angle along with energy gain or energy loss of the neutrons on passage through a sample is interpreted in terms of the motion of particles in the sample.

NMR longitudinal relaxation time (T_1) measurements involve a spin relaxation process that gives up energy to the surroundings. The relaxation is caused by local magnetic fields that arise from the tumbling motion of molecules in a fluid sample and the relaxation times can be interpreted in terms of the mobilities of molecules. It has been shown that big molecules in viscous fluids typically rotate in a series of small steps of about 5°, whereas small molecules in non-viscous fluids typically jump through about 57° in each step. Another fact of basic interest is that proton and ^{17}O NMR measurements show that the time characteristic of protons hopping from one molecule to the next is about 1.5 ps, which is comparable to the time that inelastic neutron scattering shows it takes a water molecule to reorientate through about 1 rad. NMR spin relaxation time measurement and relationships to molecular motion are discussed in Section 14.9.

When the laser beam of dynamic light-scattering measurements scatters off two molecules, the intensity at the detector may be high or low, depending on the degree of constructive and destructive interference. Since the detector signal depends on scattering from a great many molecules, the resulting light intensity fluctuation is interpreted as depending on the diffusion coefficient, which is a measure of the rate of molecular motion.

Solutions to exercises

E20.1(b)

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \; [20.7] \quad \text{and} \quad c = \langle v^2 \rangle^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} \; [20.3]$$

The mean translational kinetic energy is: $\langle E_k \rangle_m = \langle \tfrac{1}{2}mv^2 \rangle N_A = \tfrac{1}{2}mN_A\langle v^2 \rangle = \tfrac{1}{2}Mc^2 = \tfrac{3}{2}RT$

The ratios of species 1 to species 2 at the same temperature are:

$$\frac{\bar{c}_1}{\bar{c}_2} = \left(\frac{M_2}{M_1}\right)^{1/2} \quad \text{and} \quad \frac{\langle E_k \rangle_1}{\langle E_k \rangle_2} = 1$$

(a) $$\frac{\bar{c}_{He}}{\bar{c}_{Hg}} = \left(\frac{200.6}{4.003}\right)^{1/2} = \boxed{7.079}$$

(b) The mean translation kinetic energy is independent of molecular mass and depends on temperature alone! Consequently, because the mean translational kinetic energy for a gas is proportional to T, the ratio of mean translational kinetic energies for gases at the same temperature always equals 1.

E20.2(b) (a)

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \; [20.7]$$

$$= \left\{\frac{8 \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})}{\pi \times (28.02 \times 10^{-3} \text{ kg mol}^{-1})}\right\}^{1/2}$$

$$= \boxed{475 \text{ m s}^{-1}}$$

(b) $$\lambda = \frac{kT}{2^{1/2}\sigma p} \text{ [see note below]} = \frac{kT}{2^{1/2}\pi d^2 p} \quad \left[\sigma = \pi d^2\right]$$

$$= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{2^{1/2}\pi \times (395 \times 10^{-12} \text{ m})^2 \times (1 \times 10^{-9} \text{ Torr}) \times (1.333 \times 10^2 \text{ Pa Torr}^{-1})} \; [1 \text{ Pa} = 1 \text{ J m}^{-3}]$$

$$= 4.45 \times 10^4 \text{ m} = \boxed{45.5 \text{ km}}$$

The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure.

(c) $$z = \frac{\bar{c}_{\text{rel}}}{\lambda}\,[20.12] = \frac{\sqrt{2}\,\bar{c}}{\lambda}\,[20.9]$$

$$= \frac{\sqrt{2}\times(475\ \text{m s}^{-1})}{4.45\times10^{4}\ \text{m}} = 1.51\times10^{-2}\ \text{s}^{-1} = \boxed{54.3\ \text{h}^{-1}}$$

Note: The standard, simple kinetic model expression for the mean free path λ estimates that a molecule moving with the mean speed $\bar{c}$ spends a mean time of $1/z$ between collisions, where z is the collision frequency [20.11a,b]. (See the IUPAC Compendium of Chemical Terminology in the IUPAC Gold Book; http://goldbook.iupac.org/.) Thus, the model estimates that

$$\lambda = \frac{\bar{c}}{z}\,[20.12\ \text{alternative}] = \frac{kT}{2^{1/2}\sigma p}\,[20.13\ \text{alternative}]$$

We use this definition throughout our computations.

E20.3(b) The Maxwell distribution of speeds is $f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^{2}\mathrm{e}^{-Mv^{2}/2RT}$ [20.4]

The factor $M/2RT$ can be evaluated as

$$\frac{M}{2RT} = \frac{44.01\times10^{-3}\ \text{kg mol}^{-1}}{2\times(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1})\times(300\ \text{K})} = 8.82\times10^{-6}\ \text{m}^{-2}\,\text{s}^{2}$$

$f(v)$ varies over the range 200 to 250 m s^{-1}. The range is large enough that the assumption of the constancy of f over the range may lead to a degree of computational error. Nonetheless, we make this assumption and then compare the answer to a software numerical integration without the assumption. First, making the assumption of the constancy of f over the integration range, we estimate the value of f to be its value at the centre of the range:

$$f(225\ \text{m s}^{-1}) = (4\pi)\times\left(\frac{8.82\times10^{-6}\ \text{m}^{-2}\,\text{s}^{2}}{\pi}\right)^{3/2}\times(225\ \text{m s}^{-1})^{2}\times \mathrm{e}^{(-8.82\times10^{-6})\times(225)^{2}}$$

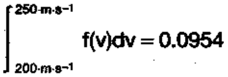
$$= 1.91\times10^{-3}\ \text{m}^{-1}\,\text{s}$$

Therefore, the fraction of molecules in the specified range is

$$\int_{v_{\text{low}}}^{v_{\text{high}}} f\mathrm{d}v\ [20.5] = f\int_{v_{\text{low}}}^{v_{\text{high}}}\mathrm{d}v = f\times\Delta v = (1.91\times10^{-3}\ \text{m}^{-1}\,\text{s})\times(50\ \text{m s}^{-1})$$

$$= \boxed{9.55\times10^{-2}}$$

corresponding to 9.6%. Here is the result of a Mathcad software numerical integration:



$$\int_{200\cdot\text{m}\cdot\text{s}^{-1}}^{250\cdot\text{m}\cdot\text{s}^{-1}} \text{f(v)dv} = 0.0954$$

In this case, the constancy assumption gives a very good result.

E20.4(b) We want to find a relationship between $c = \langle v^2\rangle^{1/2} = (3RT/M)^{1/2}$ [20.2, 20.3] and $\langle v^4\rangle^{1/4}$ for a perfect gas. We begin by finding an expression for $\langle v^4\rangle$:

$$\langle v^4\rangle = \int_0^\infty v^4 f(v)\mathrm{d}v = 4\pi(M/2\pi RT)^{3/2}\int_0^\infty v^6\mathrm{e}^{-Mv^2/2RT}\mathrm{d}v \text{ [20.4]}$$

$$= 4\pi(M/2\pi RT)^{3/2}\left\{\frac{15\pi^{1/2}}{16}\left(\frac{2RT}{M}\right)^{7/2}\right\}\text{[standard integral]}$$

$$= 15\left(\frac{RT}{M}\right)^2$$

Thus, $\langle v^4\rangle/\langle v^2\rangle^2 = 5/3$ or $\boxed{\langle v^4\rangle^{1/4}/\langle v^2\rangle^{1/2} = (5/3)^{1/4}}$.

E20.5(b) We want the pressure at which $\lambda = d$ where the atomic diameter, d, of an argon atom is related to the collision cross-section by $\sigma = \pi d^2$ or $d = (\sigma/\pi)^{1/2}$.

$$p = \frac{kT}{2^{1/2}\sigma\lambda}\text{[Exercise 20.2(b) note]} = \frac{kT}{2^{1/2}\sigma\times(\sigma/\pi)^{1/2}} = \left(\frac{\pi}{2}\right)^{1/2}\frac{kT}{\sigma^{3/2}}$$

$$= \left(\frac{\pi}{2}\right)^{1/2}\frac{(1.381\times10^{-23}\text{ J K}^{-1})\times(298\text{ K})}{(0.36\times10^{-18}\text{ m}^2)^{3/2}}\text{[Table 20.1]}$$

$$= 2.39\times10^7\text{ Pa} = \boxed{239\text{ bar}}\text{ [1 J = 1 Pa m}^3\text{]}$$

This pressure is somewhat higher than the ~150 bar compressed gas cylinder in which argon gas is normally purchased. It should be recognized that at this high pressure the perfect gas estimate may be in error.

E20.6(b)
$$\lambda = \frac{kT}{2^{1/2}\sigma p}\text{[Exercise 20.2(b) note]}$$

$$= \frac{(1.381\times10^{-23}\text{ J K}^{-1})\times(217\text{ K})}{(2^{1/2})\times(0.43\times10^{-18}\text{ m}^2)\times(12.1\times10^3\text{ Pa})} = \boxed{0.41\ \mu\text{m}}$$

E20.7(b) At an altitude of 15 km the temperature is 217 K and the pressure is 12.1 kPa:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}\text{ [20.7]}$$

$$= \left\{\frac{8\times(8.3145\text{ J mol}^{-1}\text{ K}^{-1})\times(217\text{ K})}{\pi\times(28.02\times10^{-3}\text{ kg mol}^{-1})}\right\}^{1/2}$$

$$= 405\text{ m s}^{-1}$$

$$z = \frac{2^{1/2}\sigma\bar{c}p}{kT}\text{ [20.11b and 20.9]}$$

$$= \frac{2^{1/2}\times(0.43\times10^{-18}\text{ m}^2)\times(405\text{ m s}^{-1})\times(12.1\times10^3\text{ Pa})}{(1.381\times10^{-23}\text{ J K}^{-1})\times(217\text{ K})}\text{[Table 20.1]}$$

$$= \boxed{9.9\times10^8\text{ s}^{-1}}$$

E20.8(b) $$\lambda = \frac{kT}{2^{1/2}\sigma p} \text{ [Exercise 20.2(b) note]}$$

$$= \frac{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298.15\ \mathrm{K})}{(2^{1/2})\times(0.52\times10^{-18}\ \mathrm{m^2})\times(p)}$$

$$= \frac{5.6\bar{0}\times10^{-3}\ \mathrm{m}}{(p/\mathrm{Pa})} = \frac{5.5\bar{3}\times10^{-8}\ \mathrm{m}}{p/\mathrm{atm}} = \frac{4.2\bar{0}\times10^{-5}\ \mathrm{m}}{p/\mathrm{Torr}} = \frac{5.6\bar{0}\times10^{-8}\ \mathrm{m}}{p/\mathrm{bar}}$$

(a) When $p = 15$ atm, $\lambda = 3.7\times10^{-9}\ \mathrm{m} = \boxed{3.7\ \mathrm{nm}}$.

(b) When $p = 1$ bar, $\lambda = 5.6\times10^{-8}\ \mathrm{m} = \boxed{56\ \mathrm{nm}}$.

(c) When $p = 1.0$ Torr, $\lambda = 4.2\times10^{-5}\ \mathrm{m} = \boxed{42\ \mu\mathrm{m}}$.

E20.9(b) $$A = (3.5\ \mathrm{cm})\times(4.0\ \mathrm{cm}) = 1.4\times10^{-5}\ \mathrm{m^2}$$

The collision frequency of the helium gas molecules with surface area A equals $Z_W A$:

$$Z_W A = \frac{pN_A}{(2\pi MRT)^{1/2}}A \text{ [20.16]}$$

$$= \frac{(111\ \mathrm{Pa})\times(6.022\times10^{23}\ \mathrm{mol^{-1}})\times(1.4\times10^{-5}\ \mathrm{m^2})}{\{2\pi(4.00\times10^{-3}\ \mathrm{kg\ mol^{-1}})\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(1500\ \mathrm{K})\}^{1/2}}$$

$$= 5.2\bar{9}\times10^{19}\ \mathrm{s^{-1}}$$

The number of helium molecule collisions within A in time interval t equals $Z_W At$ if p does not change significantly during the period t:

$$Z_W At = (5.2\bar{9}\times10^{19}\ \mathrm{s^{-1}})\times(10\ \mathrm{s}) = \boxed{5.3\times10^{20}}$$

E20.10(b) The mass loss equals the effusion mass loss multiplied by the time period t:

$$m_{\text{loss}} = (\text{rate of effusion})\times t\times m = (\text{rate of effusion})\times t\times M/N_A$$

$$m_{\text{loss}} = \left(\frac{pA_0N_A}{(2\pi MRT)^{1/2}}\right)\times\left(\frac{Mt}{N_A}\right) \text{[20.16]}$$

$$= pA_0t\times\left(\frac{M}{2\pi RT}\right)^{1/2}$$

$$= (0.224\ \mathrm{Pa})\times\{\pi(1.50\times10^{-3}\ \mathrm{m})^2\}\times(24\times3600\ \mathrm{s})\times\left(\frac{0.300\ \mathrm{kg\ mol^{-1}}}{2\pi(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(450\ \mathrm{K})}\right)^{1/2}$$

$$= \boxed{0.489\ \mathrm{g}}$$

E20.11(b) The mass loss equals the effusion mass loss multiplied by the time period t:

$$m_{\text{loss}} = (\text{rate of effusion})\times t\times m = (\text{rate of effusion})\times t\times M/N_A$$

$$m_{\text{loss}} = \left(\frac{pA_0N_A}{(2\pi MRT)^{1/2}}\right)\times\left(\frac{Mt}{N_A}\right)\text{[20.16]} = pA_0t\times\left(\frac{M}{2\pi RT}\right)^{1/2}$$

Solving for p gives

$$p = \frac{m_{\text{loss}}}{A_0 t}\left(\frac{2\pi RT}{M}\right)^{1/2}$$

$$= \frac{277\times10^{-6}\,\text{kg}}{\{\pi(0.25\times10^{-3}\,\text{m})^2\}\times(500\,\text{s})}\left(\frac{2\pi(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})\times(573\,\text{K})}{0.200\,\text{kg mol}^{-1}}\right)^{1/2}$$

$$= \boxed{1.09\times10^3\,\text{Pa}}$$

E20.12(b) The pressure of this exercise changes significantly during time period t so it is useful to spend a moment finding an expression for $p(t)$. Mathematically, the rate of effusion is the derivative $-\mathrm{d}N/\mathrm{d}t$. Substitution of the perfect gas law for N, $N = pVN_A/RT$, where V and T are constants, reveals that the rate of effusion can be written as $-(N_A V/RT)\mathrm{d}p/\mathrm{d}t$. This formulation of the rate of effusion, along with eqn 20.16, is used to find $p(t)$:

$$-\left(\frac{N_A V}{RT}\right)\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{pA_0N_A}{(2\pi MRT)^{1/2}}\ [20.16]$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{pA_0}{V}\left(\frac{RT}{2\pi M}\right)^{1/2}$$

$$\frac{\mathrm{d}p}{p} = -\frac{\mathrm{d}t}{\tau},\quad \text{where}\quad \tau = \frac{V}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2}$$

$$\int_{p_0}^{p}\frac{\mathrm{d}p}{p} = -\frac{1}{\tau}\int_0^t \mathrm{d}t,\quad \text{where } p_0 \text{ is the initial pressure}$$

$$\ln\frac{p}{p_0} = -\frac{t}{\tau}\quad \text{or}\quad p(t) = p_0\mathrm{e}^{-t/\tau}$$

The nitrogen and unknown fluorocarbon data can be used to determine the relaxation time, τ, for each:

$$\tau_{\text{unk}} = \frac{t_{\text{unk}}}{\ln(p_0/p)_{\text{unk}}} = \frac{82.3\,\text{s}}{\ln(65.1/42.1)} = 189\,\text{s}$$

$$\tau_{N_2} = \frac{t_{N_2}}{\ln(p_0/p)_{N_2}} = \frac{18.5\,\text{s}}{\ln(65.1/42.1)} = 42.4\,\text{s}$$

The above definition of τ shows that it is proportional to $M^{1/2}$. Since the ratio of the relaxation times cancels the constant of proportionality,

$$\left(\frac{M_{\text{unk}}}{M_{N_2}}\right)^{1/2} = \frac{\tau_{\text{unk}}}{\tau_{N_2}}$$

$$M_{\text{unk}} = \left(\frac{\tau_{\text{unk}}}{\tau_{N_2}}\right)^2 M_{N_2}$$

$$= \left(\frac{189}{42.4}\right)^2 \times (28.02\,\text{g mol}^{-1}) = \boxed{557\,\text{g mol}^{-1}}$$

E20.13(b) In Exercise 20.12b it is shown that

$$\ln\frac{p}{p_0} = -\frac{t}{\tau} \quad \text{or} \quad p(t) = p_0 e^{-t/\tau}, \quad \text{where} \quad \tau = \frac{V}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2}$$

The relaxation time, τ, of nitrogen is calculated with the data:

$$\tau = \left(\frac{22.0\ \text{m}^3}{\pi(0.050\times10^{-3}\ \text{m})^2}\right)\times\left\{\frac{2\pi(28.02\times10^{-3}\ \text{kg mol}^{-1})}{(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})\times(293\ \text{K})}\right\}^{1/2} = 2.4\times10^{7}\ \text{s} = 27\overline{6}\ \text{days}$$

The time required for the specified pressure decline is calculated with the above equation.

$$t = \tau\ln(p_0/p) = (27\overline{6}\ \text{days})\times\ln(122/105) = \boxed{41.\overline{4}\ \text{days}}$$

E20.14(b) The flux is

$$J = -\kappa\frac{dT}{dz}[20.20] = -\tfrac{1}{3}\lambda\bar{c}C_{V,\text{m}}[\text{A}]\frac{dT}{dz}[20.23] = -\frac{\tfrac{1}{3}\lambda\bar{c}C_{V,\text{m}}p}{RT}\frac{dT}{dz}[\text{perfect gas, }[\text{A}] = p/RT]$$

where the negative sign indicates flow toward lower temperature and

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}[20.7] \quad \text{and} \quad \lambda = \frac{kT}{2^{1/2}\sigma p}[\text{Exercise 20.2(b) note}] = \frac{RT}{2^{1/2}N_{\text{A}}\sigma p}$$

$$J = -\tfrac{1}{3}\left(\frac{RT}{2^{1/2}N_{\text{A}}\sigma p}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}\times\left(\frac{C_{V,\text{m}}p}{RT}\right)\times\frac{dT}{dz}$$

$$= -\tfrac{2}{3}\times\left(\frac{RT}{\pi M}\right)^{1/2}\times\left(\frac{C_{V,\text{m}}}{N_{\text{A}}\sigma}\right)\times\frac{dT}{dz}$$

For hydrogen $M = 2.016\ \text{g mol}^{-1}$, $\sigma = 0.27\ \text{nm}^2$ [Table 20.1], and appendix data tables are used to calculate $C_{V,\text{m}}$: $C_{V,\text{m}} = C_{p,\text{m}} - R = (28.824 - 8.3145)\ \text{J K}^{-1}\,\text{mol}^{-1} = 20.510\ \text{J K}^{-1}\ \text{mol}^{-1}$.

$$J = -\frac{2}{3}\times\left(\frac{(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1})\times(260\ \text{K})}{\pi\times(2.016\times10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2}$$

$$\times\left\{\frac{20.510\ \text{J K}^{-1}\,\text{mol}^{-1}}{(6.022\times10^{23}\ \text{mol}^{-1})\times(0.27\times10^{-18}\ \text{m}^2)}\right\}\times(3.5\ \text{K m}^{-1})$$

$$= \boxed{-0.17\ \text{J m}^{-2}\,\text{s}^{-1}}$$

E20.15(b) The coefficient of thermal conductivity, κ, is a function of the mean free path, λ, which in turn is a function of the collision cross-section, σ. Hence, reversing the order, σ can be obtained from κ:

$$\kappa = \tfrac{1}{3}\lambda\bar{c}C_{V,\text{m}}[\text{A}]\,[20.23] \quad \text{and} \quad \bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}[20.7]$$

$$\lambda = \frac{kT}{2^{1/2}\sigma p}[\text{Exercise 20.2(b) note}] = \frac{1}{2^{1/2}\sigma N_{\text{A}}[\text{A}]}\left[\frac{p}{kT} = N_{\text{A}}[\text{A}]\right]$$

Therefore, $\kappa = \dfrac{\bar{c}C_{V,\mathrm{m}}}{3\times 2^{1/2}\sigma N_\mathrm{A}}$ or $\sigma = \dfrac{\bar{c}C_{V,\mathrm{m}}}{3\times 2^{1/2}N_\mathrm{A}\kappa}$

For nitrogen at 298 K, $\bar{c} = \left\{\dfrac{8\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{\pi\times(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}})}\right\}^{1/2} = 475\ \mathrm{m\ s^{-1}}$.

From Table 20.2 thermal conductivity values at 273 K we estimate the value at 298 K using the kinetic theory finding the $\kappa \propto T^{1/2}$ [20.23]: $\kappa = (0.0240\ \mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}})\times(298/273)^{1/2} = 0.0251\ \mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}}$.

The $C_{V,\mathrm{m}}$ value is calculated with the perfect gas relationship $C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R$ and the $C_{p,\mathrm{m}}$ value provided in an appendix table ($29.125\ \mathrm{J\ K^{-1}\ mol^{-1}}$). This gives $C_{V,\mathrm{m}} = 20.811\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Alternatively, the $C_{V,\mathrm{m}}$ value is calculated with the equipartition theorem: $C_{V,\mathrm{m}} = \frac{5}{2}R = 20.786\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

$$\begin{aligned}\sigma &= \frac{(475\ \mathrm{m\ s^{-1}})\times(20.811\ \mathrm{J\ K^{-1}\ mol^{-1}})}{3\times2^{1/2}\times(6.022\times10^{23}\ \mathrm{mol^{-1}})\times(0.0251\ \mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}})}\\ &= 1.54\times10^{-19}\ \mathrm{m^2}\\ &= \boxed{0.154\ \mathrm{nm^2}}\end{aligned}$$

The experimental value is $0.43\ \mathrm{nm^2}$.

Question. What approximations inherent in the equation used in the solution to this exercise are the likely cause of the factor of 2.8 difference between the experimental and calculated values of the collision cross-section for neon?

E20.16(b) The thermal energy flux ('heat' flux) is described by: $J(\text{energy}) = -\kappa\dfrac{\mathrm{d}T}{\mathrm{d}z}\,[20.20]$, where the negative sign indicates flow toward lower temperature. This is the rate of energy transfer per unit area. The total rate of energy transfer across area A is

$$\frac{\mathrm{d}E}{\mathrm{d}t} = AJ(\text{energy}) = -\kappa A\frac{\mathrm{d}T}{\mathrm{d}z}$$

To calculate the temperature gradient with the given data, we assume that the gradient is in a steady state. Then, recognizing that temperature differences have identical magnitude in Celsius or Kelvin units,

$$\begin{aligned}\frac{\mathrm{d}T}{\mathrm{d}z} &= \frac{\Delta T}{\Delta z} = \frac{\{(-10)-(50)\}\ \mathrm{K}}{10.0\times10^{-2}\ \mathrm{m}}\\ &= -6.0\times10^{2}\ \mathrm{K\ m^{-1}}\end{aligned}$$

We now assume that the coefficient of thermal conductivity of the gas between the window panes is comparable to that of nitrogen given in Table 20.2: $\kappa \approx 0.0240\ \mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}}$.

Therefore, the rate of energy transfer, the rate of heat loss, towards the low temperature is

$$\begin{aligned}\frac{\mathrm{d}E}{\mathrm{d}t} &\approx -(0.0240\ \mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}})\times(1.50\ \mathrm{m^2})\times(-6.0\times10^{2}\ \mathrm{K\ m^{-1}})\\ &\approx 22\ \mathrm{J\ s^{-1}}\\ &= \boxed{22\ \mathrm{W}}\end{aligned}$$

E20.17(b) $\eta = \frac{1}{3}M\lambda\bar{c}p/RT$ [20.24, [A] = p/RT for a perfect gas]

We begin by substituting kinetic-theory relationships for λ [E20.2(b) note] and $\bar{c}$ [20.7]:

$$\eta = \tfrac{1}{3}M \times \left(\frac{RT}{2^{1/2}\sigma N_A p}\right) \times \left(\frac{8RT}{\pi M}\right)^{1/2} \times \left(\frac{p}{RT}\right)$$

$$= \left(\frac{M}{3 \times 2^{1/2}\sigma N_A}\right) \times \left(\frac{8RT}{\pi M}\right)^{1/2}$$

We now solve, and compute, the collision cross-section for nitrogen at 273 K:

From Table 20.2, $\eta = 166 \times 10^{-6}\,\text{P} = 166 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1}$:

$$\sigma = \left\{\frac{28.02 \times 10^{-3}\,\text{kg mol}^{-1}}{3 \times 2^{1/2} \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \times (166 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1})}\right\}$$

$$\times \left\{\frac{8(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})}{\pi(28.02 \times 10^{-3}\,\text{kg mol}^{-1})}\right\}^{1/2}$$

$$= 3.00 \times 10^{-19}\,\text{m}^2 = \boxed{0.300\,\text{nm}^2}$$

E20.18(b) The flow rate of a compressible gas in a steady state, Newtonian, laminar flow through a pipe of radius R and length l is described by Poiseuille's formula,

$$\frac{dV}{dt} = \frac{(p_1^2 - p_2^2)\pi R^4}{16 l \eta p_0}$$

where V is the volume flowing, p_1 and p_2 are pressures at each end of the tube, and p_0 is the pressure at which the volume is measured. (This formula is derived below.) Solving for p_1^2 gives

$$p_1^2 = p_2^2 + \left(\frac{16 l \eta p_0}{\pi R^4}\right) \times \left(\frac{dV}{dt}\right)$$

$$= (1.00 \times 10^5)^2\,\text{Pa}^2 + \left(\frac{(16) \times (10.50\,\text{m}) \times (176 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1}) \times (1.00 \times 10^5\,\text{Pa})}{\pi \times (7.5 \times 10^{-3}\,\text{m})^4}\right)$$

$$\times (8.70 \times 10^{-6}\,\text{m s}^{-1})$$

$$= 1.0000259 \times 10^{10}\,\text{Pa}^2$$

Hence, $p_1 = \boxed{1.0000129\,\text{bar}}$

COMMENT. For the exercise as stated the answer is not sensitive to the viscosity. The flow rate is so low that the inlet pressure would equal the outlet pressure (to the precision of the data) whether the viscosity were that of N_2 at 300 K or 293 K, or even liquid water at 293 K!

To begin the derivation of the Poiseuille formula consider eqn 20.21 in the form applicable to flow through a cylinder of radius r, where $0 \le r \le R$: $J(x\text{ component of momentum}) = -\eta \times (dv_x/dr)$ with x parallel to the tube walls. This momentum flux is the increase in momentum along the radius per time t per area of cylinder surface. As such, the force acting in the x direction is given by

$$(2\pi r l) \times J(x\text{ component of momentum}) = -2\pi r l \eta \times (dv_x/dr)$$

This force is also given by the pressure difference between the cylinder ends, which is taken to be a constant along the radius with a constant gradient along x so that $(p_2 - p_1)/l = \mathrm{d}p/\mathrm{d}x$, multiplied by the area cross-section of the cylinder: $-\pi r^2(p_2 - p_1)$. Steady, laminar flow requires that these two forces balance. Thus, in this flow model we envision a maximum of flow at $r = 0$ with decreasing flow until it is zero at $r = R$ because of the viscous drag on the surface of each cylinder due to friction with more slowly moving surrounding gas. Equating the two forces and solving for $\mathrm{d}v_x$ gives

$$-2\pi r l\eta \times (\mathrm{d}v_x/\mathrm{d}r) = -(p_2 - p_1)\pi r^2$$

$$\mathrm{d}v_x = \frac{1}{2\eta}\frac{\mathrm{d}p}{\mathrm{d}x}r\mathrm{d}r$$

Now, the volume size of a cylinder of length $\mathrm{d}x$ is given by $\mathrm{d}V = \pi r^2\mathrm{d}x$, so $\mathrm{d}x/\mathrm{d}t = (1/\pi r^2)\mathrm{d}V/\mathrm{d}t$. Equating $\mathrm{d}x/\mathrm{d}t$ with $\mathrm{d}v_x$ in our working equation gives

$$\mathrm{d}\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right) = \frac{\pi}{2\eta}\frac{\mathrm{d}p}{\mathrm{d}x}r^3\mathrm{d}r$$

and integration from $r = 0$ to $r = R$ with no contribution to the gas flow at $r = R$ gives

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{\pi R^4}{8\eta}\frac{\mathrm{d}p}{\mathrm{d}x}$$

To assure conservation of mass in a gaseous volume that expands while moving toward the low-pressure end, we make the substitution $V = nRT/p$ to get

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\pi R^4 p}{8\eta RT}\frac{\mathrm{d}p}{\mathrm{d}x} = -\frac{\pi R^4}{16\eta RT}\frac{\mathrm{d}p^2}{\mathrm{d}x}, \quad \text{where} \quad \frac{\mathrm{d}p^2}{\mathrm{d}x} = \frac{p_2^2 - p_1^2}{l}$$ because the pressure gradient is independent of x.

If we measure the amount of gas at $p = p_0$, we can make the substitution $\mathrm{d}n = (p_0/RT)\mathrm{d}V$ to get a gas flow of

$$\boxed{\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\pi R^4}{16\eta p_0 l}(p_1^2 - p_2^2)\ \text{Poiseuille's formula}}$$

E20.19(b) $\eta = \tfrac{1}{3}M\lambda\bar{c}[\mathrm{A}]\,[20.24] = \left(\frac{1}{3\sigma N_\mathrm{A}}\right) \times \left(\frac{4MRT}{\pi}\right)^{1/2}$ [Exercise 20.2(b) note, 20.7, $[\mathrm{A}] = p/RT$]

$$\eta = \left(\frac{1}{3 \times (0.88 \times 10^{-18}\,\mathrm{m}^2) \times (6.022 \times 10^{23}\,\mathrm{mol}^{-1})}\right)$$

$$\times \left\{\frac{4 \times (78.11 \times 10^{-3}\,\mathrm{kg\,mol}^{-1}) \times (8.3145\,\mathrm{J\,K}^{-1}\,\mathrm{mole}^{-1}) \times T}{\pi}\right\}^{1/2}$$

$$= (5.7\bar{2} \times 10^{-7}\,\mathrm{kg\,m}^{-1}\mathrm{s}^{-1}) \times (T/\mathrm{K})^{1/2} = (5.7\bar{2}\,\mu\mathrm{P}) \times (T/\mathrm{K})^{1/2}$$

(a) At $T = 273$ K, $\eta = (5.7\bar{2}\,\mu\mathrm{P}) \times (273)^{1/2} = \boxed{95.\bar{5}\,\mu\mathrm{P}}$

(b) At $T = 298$ K, $\eta = (5.7\bar{2}\,\mu\mathrm{P}) \times (298)^{1/2} = \boxed{98.\bar{7}\,\mu\mathrm{P}}$

(c) At $T = 1000$ K, $\eta = (5.7\bar{2}\,\mu\mathrm{P}) \times (1000)^{1/2} = \boxed{18\bar{1}\,\mu\mathrm{P}}$

E20.20(b) $$\kappa = \tfrac{1}{3}\lambda\bar{c}C_{V,\mathrm{m}}[\mathrm{A}]\,[20.23] = \left(\frac{C_{V,\mathrm{m}}}{3\sigma N_{\mathrm{A}}}\right)\times\left(\frac{4RT}{\pi M}\right)^{1/2} \quad [\text{Exercise 20.2(b) note, 20.7, } [\mathrm{A}] = p/RT]$$

According to the equipartition theorem $C_{V,\mathrm{m}} = \tfrac{3}{2}R = \tfrac{3}{2}kN_{\mathrm{A}}$ for a monatomic gas so

$$\kappa = \left(\frac{k}{2\sigma}\right)\times\left(\frac{4RT}{\pi M}\right)^{1/2}$$

$$= \left(\frac{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}}{2}\right)\times\left(\frac{4\times(8.3145\ \mathrm{J\ K^{-1}\,mol^{-1}})\times(300\ \mathrm{K})}{\pi}\right)^{1/2}$$

$$\times\left(\frac{1}{(10^{-18}\ \mathrm{m^2})\times\sigma/\mathrm{nm}^2}\right)\times\left(\frac{1}{(10^{-3}\ \mathrm{kg\ mol^{-1}})\times(M/\mathrm{g\ mol^{-1}})}\right)^{1/2}$$

$$= (0.0123\ \mathrm{J\ K^{-1}\,m^{-1}\,s^{-1}})\times\left(\frac{1}{\sigma/\mathrm{nm}^2}\right)\times\left(\frac{1}{M/\mathrm{g\ mol^{-1}}}\right)^{1/2} \quad \text{at} \quad T = 300\ \mathrm{K}$$

$$\begin{aligned} J_{\text{energy}} &= -\kappa\,\mathrm{d}T/\mathrm{d}z\ [20.20] = -\kappa\Delta T/\Delta z\ [\text{steady-state flux}] \\ &= -\kappa\times(305\ \mathrm{K} - 295\ \mathrm{K})/(0.15\ \mathrm{m}) \\ &= -(66.\overline{7}\ \mathrm{K\ m^{-1}})\kappa, \text{ where the negative indicates an energy flux toward the low temperature} \end{aligned}$$

(a) For neon:

$$\kappa = (0.0123\ \mathrm{J\ K^{-1}\,m^{-1}\,s^{-1}})\times\left(\frac{1}{0.24}\right)\times\left(\frac{1}{20.18}\right)^{1/2} = \boxed{11.\overline{4}\ \mathrm{mJ\ K^{-1}\,m^{-1}\,s^{-1}}}$$

The observed value of κ is larger by a factor of 4.

$$J_{\text{energy}} = -(66.\overline{7}\ \mathrm{K\ m^{-1}})\times(11.\overline{4}\ \mathrm{mJ\ K^{-1}\,m^{-1}\,s^{-1}}) = \boxed{-0.76\ \mathrm{W\ m^{-2}}}$$

$$\text{Rate of energy flow} = J_{\text{energy}}A = (-0.76\ \mathrm{W\ m^{-2}})\times(0.0225\ \mathrm{m^2}) = \boxed{-17\ \mathrm{mW}}$$

The negative sign indicates flow toward the low temperature.

(b) For dinitrogen the equipartition theorem gives $C_{V,\mathrm{m}} = \tfrac{5}{2}R$. Consequently, the above equation for the thermal conductivity must be increased by a factor of $\tfrac{5}{3}$.

$$\kappa = \left(\tfrac{5}{3}\right)\times(0.0123\ \mathrm{J\ K^{-1}\,m^{-1}\,s^{-1}})\times\left(\frac{1}{0.43}\right)\times\left(\frac{1}{28.02}\right)^{1/2} = \boxed{9.0\ \mathrm{mJ\ K^{-1}\,m^{-1}\,s^{-1}}}$$

The observed value of κ is larger by a factor of 2.7.

$$J_{\text{energy}} = -(66.\overline{7}\ \mathrm{K\ m^{-1}})\times(9.0\ \mathrm{mJ\ K^{-1}\,m^{-1}\,s^{-1}}) = \boxed{-0.60\ \mathrm{W\ m^{-2}}}$$

$$\text{Rate of energy flow} = J_{\text{energy}}A = (-0.60\ \mathrm{W\ m^{-2}})\times(0.0225\ \mathrm{m^2}) = \boxed{-14\ \mathrm{mW}}$$

The negative sign indicates flow toward the low temperature.

COMMENT. The computations of simple kinetic theory give an estimate for the coefficient of thermal conductivity that is low but satisfying in that its simplicity gives a result within an order of magnitude of being correct. To improve the estimate requires removal of the hard-sphere assumption with consideration of more realistic forces of attraction and repulsion. Additionally, the simple utilization of a mean speed has to be replaced with a kinetic theory that recognizes that faster molecules transport more kinetic energy than do slower ones.

E20.21(b)

$$\kappa=\tfrac{1}{3}\lambda\bar{c}C_{V,\mathrm{m}}[\mathrm{A}]\,[20.23]=\left(\frac{C_{V,\mathrm{m}}}{3\sigma N_{\mathrm{A}}}\right)\times\left(\frac{4RT}{\pi M}\right)^{1/2}\ [\text{Exercise 20.2(b) note, 20.7, }[\mathrm{A}]=p/RT]$$

$$=\left(\frac{20.8\ \mathrm{J\ K^{-1}\ mol^{-1}}}{3\times(0.43\times10^{-18}\ \mathrm{m^2})\times(6.022\times10^{23}\ \mathrm{mol^{-1}})}\right)\times\left(\frac{4\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(293\ \mathrm{K})}{\pi\times(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}})}\right)^{1/2}$$

$$=\boxed{8.9\ \mathrm{mJ\ K^{-1}\ m^{-1}\ s^{-1}}}$$

Question. Can the differences between the calculated and experimental values of κ be accounted for by the difference in temperature (293 K here, 273 K in Table 20.2)? If not, what might be responsible for the difference?

E20.22(b)

$$D=\tfrac{1}{3}\lambda\bar{c}\,[20.22]=\tfrac{1}{3}\left(\frac{kT}{2^{1/2}\sigma p}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}\ [\text{Exercise 20.2(b) note, 20.7}]$$

$$=\tfrac{1}{3}\left(\frac{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})}{2^{1/2}\times(0.43\times10^{-18}\ \mathrm{m^2})\times p\times(1\ \mathrm{J\ m^{-3}\ Pa^{-1}})}\right)\times\left(\frac{8\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{\pi\times(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}})}\right)^{1/2}$$

$$=\frac{1.07\ \mathrm{m^2\ s^{-1}}}{p/\mathrm{Pa}}$$

The flux due to diffusion is $J=-D\left(\dfrac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)$ [20.19], where $\mathcal{N}$ is the number density and z is the direction of the pressure gradient. Dividing both sides by the Avogadro constant converts $\mathcal{N}$ to molar concentration c, while converting the flux to number of moles per unit area per second. Thus, with a negative sign that indicates mass flow from high to low pressure,

$$J=-D\frac{\mathrm{d}c}{\mathrm{d}z}=-D\frac{\mathrm{d}(n/V)}{\mathrm{d}z}=-\frac{D}{RT}\frac{\mathrm{d}p}{\mathrm{d}z}\ [\text{perfect gas law}].$$

For a pressure gradient of $0.20\ \mathrm{bar\ m^{-1}}=2.0\times10^{4}\ \mathrm{Pa\ m^{-1}}$,

$$J=\frac{(2.0\times10^{4}\ \mathrm{Pa\ m^{-1}})\times D}{(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(298\ \mathrm{K})}=(8.0\bar{7}\ \mathrm{mol\ m^{-2}\ s^{-1}})\times D/(\mathrm{m^2\ s^{-1}}).$$

(a) $p=10.0\ \mathrm{Pa}$,

$$D=\frac{1.07\ \mathrm{m^2\ s^{-1}}}{10}=\boxed{0.107\ \mathrm{m^2\ s^{-1}}}\ \text{and}\ J=(8.0\bar{7}\ \mathrm{mol\ m^{-2}\ s^{-1}})\times(0.107)=\boxed{0.86\ \mathrm{mol\ m^{-2}\ s^{-1}}}$$

(b) $p=100\ \mathrm{kPa}$,

$$D=\frac{1.07\ \mathrm{m^2\ s^{-1}}}{1.00\times10^{5}}=\boxed{1.07\times10^{-5}\ \mathrm{m^2\ s^{-1}}}\ \text{and}\ J=(8.0\bar{7}\ \mathrm{mol\ m^{-2}\ s^{-1}})\times(1.07\times10^{-5})$$

$$=\boxed{86\ \mu\mathrm{mol\ m^{-2}\ s^{-1}}}$$

(c) $p = 15.0\ \text{MPa}$,

$$D = \frac{1.07\ \text{m}^2\,\text{s}^{-1}}{15.0\times10^{6}} = \boxed{7.13\times10^{-8}\ \text{m}^2\,\text{s}^{-1}}\ \text{and}\ J = (8.0\bar{7}\ \text{mol m}^{-2}\,\text{s}^{-1})\times(7.13\times10^{-8})$$

$$= \boxed{0.58\ \mu\text{mol m}^{-2}\,\text{s}^{-1}}$$

E20.23(b) The molar ionic conductivity is related to mobility by

$$\begin{aligned}\lambda_{\pm} &= zu_{\pm}F\ [20.36]\\ &= 1\times(4.24\times10^{-8}\ \text{m}^2\,\text{s}^{-1}\,\text{V}^{-1})\times(96485\ \text{C mol}^{-1})\\ &= \boxed{4.09\ \text{mS m}^2\,\text{mol}^{-1}}\end{aligned}$$

E20.24(b) $s = u\mathcal{E}\ [20.34]$ and $\mathcal{E} = \dfrac{\Delta\phi}{l}\ [20.30]$

Therefore,

$$\begin{aligned}s &= u\left(\frac{\Delta\phi}{l}\right) = (4.01\times10^{-8}\ \text{m}^2\,\text{s}^{-1}\,\text{V}^{-1})\times\left(\frac{12.0\ \text{V}}{1.00\times10^{-2}\ \text{m}}\right)\\ &= 4.81\times10^{-5}\ \text{m s}^{-1} = \boxed{48.1\ \mu\text{m s}^{-1}}\end{aligned}$$

E20.25(b) The basis for the solution is Kohlrausch's law of independent migration of ions [eqn 20.29]. The limiting molar conductivity of a dissolved salt is the sum of formula weighted limiting molar conductivities of the formula ions at infinite dilution, so

$$\Lambda^{\circ}_{\text{m}} = \nu_{+}\lambda_{+} + \nu_{-}\lambda_{-}\ [20.29]$$

$$\Lambda^{\circ}_{\text{m}}(\text{NaI}) = \lambda(\text{Na}^{+}) + \lambda(\text{I}^{-}) = 12.69\ \text{mS m}^2\,\text{mol}^{-1}$$

$$\Lambda^{\circ}_{\text{m}}(\text{NaCH}_3\text{CO}_2) = \lambda(\text{Na}^{+}) + \lambda(\text{CH}_3\text{CO}_2^{-}) = 9.10\ \text{mS m}^2\,\text{mol}^{-1}$$

$$\Lambda^{\circ}_{\text{m}}(\text{Mg(CH}_3\text{CO}_2)_2) = \lambda(\text{Mg}^{2+}) + 2\lambda(\text{CH}_3\text{CO}_2^{-}) = 18.78\ \text{mS m}^2\,\text{mol}^{-1}$$

Hence,

$$\begin{aligned}\Lambda^{\circ}_{\text{m}}(\text{MgI}_2) &= \Lambda^{\circ}_{\text{m}}(\text{Mg(CH}_3\text{CO}_2)_2) + 2\Lambda^{\circ}_{\text{m}}(\text{NaI}) - 2\Lambda^{\circ}_{\text{m}}(\text{NaCH}_3\text{CO}_2)\\ &= (18.78 + 2\times12.69 - 2\times9.10)\ \text{mS m}^2\,\text{mol}^{-1} = \boxed{25.96\ \text{mS m}^2\,\text{mol}^{-1}}\end{aligned}$$

E20.26(b) $u_{\pm} = \dfrac{\lambda_{\pm}}{zF}\ [20.36];\ z = 1;\ \text{S} = 1\ \Omega^{-1} = 1\ \text{C V}^{-1}\,\text{s}^{-1}$

$$u(\text{F}^{-}) = \frac{5.54\ \text{mS m}^2\,\text{mol}^{-1}}{9.6485\times10^{4}\ \text{C mol}^{-1}} = 5.74\times10^{-5}\ \text{mS C}^{-1}\,\text{m}^2 = \boxed{5.74\times10^{-8}\ \text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}}$$

$$u(\text{Cl}^{-}) = \frac{7.635\ \text{mS m}^2\,\text{mol}^{-1}}{9.6485\times10^{4}\ \text{C mol}^{-1}} = \boxed{7.913\times10^{-8}\ \text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}}$$

$$u(\text{Br}^{-}) = \frac{7.81\ \text{mS m}^2\,\text{mol}^{-1}}{9.6485\times10^{4}\ \text{C mol}^{-1}} = \boxed{8.09\times10^{-8}\ \text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}}$$

E20.27(b) $$D=\frac{uRT}{zF}\,[20.50];\ z=1;\ 1\ \mathrm{C\ V}=1\ \mathrm{J}$$

$$D=\frac{(4.24\times10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}})\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{1\times9.6485\times10^{4}\ \mathrm{C\ mol^{-1}}}=\boxed{1.09\times10^{-9}\ \mathrm{m^2\ s^{-1}}}$$

E20.28(b) The parabolic decay/growth in concentration c has the form $c(x)=c_0-Ax^2$, where c_0 is the concentration at $x=0$ and the constant A is determined by the condition that $c(8\ \mathrm{cm})=\frac{1}{2}c_0$.

$$A=\frac{c_0-c(x)}{x^2}=\frac{c_0-\frac{1}{2}c_0}{(8\ \mathrm{cm})^2}=(7.81\times10^{-3}\ \mathrm{cm^{-2}})\times c_0=(78.1\ \mathrm{m^{-2}})\times c_0$$

The concentration becomes negligibly small at $|x|=11.3$ cm so computations are limited to values of x for which $|x|<11.3$ cm. The thermodynamic force is determined with eqn 20.45:

$$\mathcal{F}(x)=-\frac{RT}{c}\frac{\mathrm{d}c}{\mathrm{d}x}\,[20.45]=-\frac{RT}{c}\frac{\mathrm{d}}{\mathrm{d}x}(c_0-Ax^2)=\frac{2ARTx}{c}$$

$$=\frac{2\times(78.1\ \mathrm{m^{-2}})\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})\times x}{1-(7.81\times10^{-3}\ \mathrm{cm^{-2}})\times x^2}$$

$$=\frac{(3.87\ \mathrm{kN\ mol^{-1}})\times(x/\mathrm{cm})}{1-(7.81\times10^{-3})\times(x/\mathrm{cm})^2}$$

$$\mathcal{F}(8\ \mathrm{cm})=\frac{(3.87\ \mathrm{kN\ mol^{-1}})\times8}{1-(7.81\times10^{-3})\times(8)^2}=\boxed{+61.9\ \mathrm{kN\ mol^{-1}}}$$

$$\mathcal{F}(11\ \mathrm{cm})=\frac{(3.87\ \mathrm{kN\ mol^{-1}})\times11}{1-(7.81\times10^{-3})\times(11)^2}=\boxed{+774\ \mathrm{kN\ mol^{-1}}}$$

The positive force indicates that the force points toward larger values of $|x|$ values.

E20.29(b) The Gaussian decay in concentration c has the form $c(x)=c_0\mathrm{e}^{-Ax^2}$, where c_0 is the concentration at $x=0$ and the constant A is determined by the condition that $c(10\ \mathrm{cm})=\frac{1}{2}c_0$.

$$A=\frac{\ln(c_0/c)}{x^2}=\frac{\ln2}{(10\ \mathrm{cm})^2}=(0.010\ \mathrm{cm^{-2}})\times\ln2=(1.00\ \mathrm{cm^{-1}\ m^{-1}})\times\ln2$$

The thermodynamic force is determined with eqn 20.45:

$$\mathcal{F}(x)=-\frac{RT}{c}\frac{\mathrm{d}c}{\mathrm{d}x}\,[20.45]=-\frac{RT}{c}\frac{\mathrm{d}}{\mathrm{d}x}c_0\mathrm{e}^{-Ax^2}=2ARTx$$

$$=2\times(1.00\ \mathrm{m^{-1}})\times\ln2\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(291\ \mathrm{K})\times(x/\mathrm{cm})$$

$$=(3.35\ \mathrm{kN\ mol^{-1}})\times(x/\mathrm{cm})$$

$$\mathcal{F}(10\ \mathrm{cm})=(3.35\ \mathrm{kN\ mol^{-1}})\times(10)=\boxed{33.5\ \mathrm{kN\ mol^{-1}}}$$

E20.30(b) Eqn 20.60, $\langle x^2\rangle=2Dt$, gives the mean square distance travelled in any one dimension in time t. We need the distance travelled from a point in any direction. The distinction here is the distinction between the one-dimensional and three-dimensional diffusion. The mean square three-dimensional distance can be obtained from the one-dimensional mean square distance since motions in the three directions are independent. Since $r^2=x^2+y^2+z^2$ [Pythagorean theorem],

$$\begin{aligned}\langle r^2\rangle &= \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = 3\langle x^2\rangle \text{ [independent motion]}\\ &= 3\times 2Dt\,[20.60] = 6Dt.\end{aligned}$$

Therefore, $t = \dfrac{\langle r^2\rangle}{6D} = \dfrac{(1.0\times10^{-2}\,\text{m})^2}{6\times(4.05\times10^{-9}\,\text{m}^2\,\text{s}^{-1})} = \boxed{4.1\times10^{3}\,\text{s}}$

E20.31(b) $a = \dfrac{kT}{6\pi\eta D}\,[20.52];\ 1\,\text{P} = 10^{-1}\,\text{kg m}^{-1}\,\text{s}^{-1}$

$$a = \frac{(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})}{6\pi\times(1.00\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})\times(1.055\times10^{-9}\,\text{m}^2\,\text{s}^{-1})} = 2.07\times10^{-10}\,\text{m} = \boxed{207\,\text{pm}}$$

E20.32(b) The Einstein–Smoluchowski equation [20.62] relates the diffusion constant to the jump distance λ and time τ required for a jump:

$$D = \frac{\lambda^2}{2\tau}\,[20.62], \quad \text{so} \quad \tau = \frac{\lambda^2}{2D}$$

If the jump distance is about one molecular diameter, or two effective molecular radii, then the jump distance can be obtained by use of the Stokes–Einstein equation [20.52]:

$$\lambda = 2a = 2\left(\frac{kT}{6\pi\eta D}\right)[20.52] = \frac{kT}{3\pi\eta D}$$

$$\tau = \frac{1}{2D}\times\left(\frac{kT}{3\pi\eta D}\right)^2 \quad [\eta_{\text{heptane}} = 0.386\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}, \textit{CRC Handbook Chemistry and Physics}]$$

$$= \frac{1}{2\times(3.17\times10^{-9}\,\text{m}^2\,\text{s}^{-1})}\times\left\{\frac{(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})}{3\pi\times(0.386\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})\times(3.17\times10^{-9}\,\text{m}^2\,\text{s}^{-1})}\right\}^2$$

$$= 2.01\times10^{-11}\,\text{s} = \boxed{20.1\,\text{ps}}$$

COMMENT. In the strictest sense we are dealing with three-dimensional diffusion. However, since we are assuming that only one jump occurs, it is probably an adequate approximation to use an equation derived for one-dimensional diffusion. For three-dimensional diffusion the equation analogous to eqn 20.62 is $\tau = \lambda^2/6D$.

Question. Can you derive the equation? Use an analysis similar to that described in the solution to Exercise 20.30(a) and (b).

E20.33(b) For three-dimensional diffusion we use an equation analogous to eqn 20.60 derived in Exercise 20.30(a) and (b).

$$t = \frac{\langle r^2\rangle}{6D}$$

(a) $\langle r^2\rangle = (1.0\times10^{-3}\,\text{m})^2 = 1.0\times10^{-6}\,\text{m}^2$

For iodine in benzene [data from Table 20.7]: $t = \dfrac{1.0\times10^{-6}\,\text{m}^2}{6\times(2.13\times10^{-9}\,\text{m}^2\,\text{s}^{-1})} = \boxed{78\,\text{s}}$

For sucrose in water: $t = \dfrac{1.0\times10^{-6}\,\text{m}^2}{6\times(0.522\times10^{-9}\,\text{m}^2\,\text{s}^{-1})} = \boxed{31\bar{9}\,\text{s}}$

(b) $\langle r^2\rangle = (1.0\times10^{-3}\,\mathrm{m})^2 = 1.0\times10^{-4}\,\mathrm{m}^2$

For iodine in benzene [data from Table 20.7]: $t = \dfrac{1.0\times10^{-4}\,\mathrm{m}^2}{6\times(2.13\times10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1})} = 7.8\times10^{3}\,\mathrm{s} = \boxed{2.2\,\mathrm{h}}$

For sucrose in water: $t = \dfrac{1.0\times10^{-4}\,\mathrm{m}^2}{6\times(0.522\times10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1})} = 3.2\times10^{4}\,\mathrm{s} = \boxed{8.9\,\mathrm{h}}$

Solutions to problems

Solutions to numerical problems

P20.2 In our one-dimensional problem, we can assign the v_x component of velocity a positive or a negative value when pointing to the east (E) or west (W), respectively. Speed is the absolute value of v_x so for discrete, rather than continuous, speeds the mean speed $\bar{c}$ is (in analogy to Example 20.1):

$$\bar{c} = \langle |v_x| \rangle = \sum_i^{\text{all speeds}} f_i |v_{x,i}| = \sum_i^{\text{all speeds}} \left(\tfrac{N_i}{N}\right) |v_{x,i}| = \left(\tfrac{1}{N}\right) \sum_i^{\text{all speeds}} N_i |v_{x,i}|$$

where N_i is the number having the velocity component $v_{x,i}$ and N is the total number of observations. $N = 328$ in this problem. Likewise, the root mean square speed c is given by

$$c = \langle v_x^2 \rangle^{1/2} = \left\{ \sum_i^{\text{all speeds}} f_i v_x^2 \right\}^{1/2} = \left\{ \sum_i^{\text{all speeds}} \left(\tfrac{N_i}{N}\right) v_x^2 \right\}^{1/2} = \left\{ \left(\tfrac{1}{N}\right) \sum_i^{\text{all speeds}} N_i v_x^2 \right\}^{1/2}$$

(a) Mean velocity:

$$\langle v_x \rangle = \frac{1}{328} \left\{ \begin{matrix} 40(80) + 62(85) + 53(90) + 12(95) + 2(100) \\ +38(-80) + 59(-85) + 50(-90) + 10(-95) + 2(-100) \end{matrix} \right\} \mathrm{km\,h^{-1}} = +2.67\ \mathrm{km\,h^{-1}}$$

$$= \boxed{2.67\ \mathrm{km\,h^{-1}\,E}}$$

(b) Mean speed:

$$\bar{c} = \frac{1}{328} \left\{ \begin{matrix} 40(80) + 62(85) + 53(90) + 12(95) + 2(100) \\ +38(80) + 59(85) + 50(90) + 10(95) + 2(100) \end{matrix} \right\} \mathrm{km\,h^{-1}} = \boxed{86.2\ \mathrm{km\,h^{-1}}}$$

(c) Root mean square speed:

$$c = \left(\frac{1}{328}\right)^{1/2} \left\{ \begin{matrix} 40(80)^2 + 62(85)^2 + 53(90)^2 + 12(95)^2 + 2(100)^2 \\ +38(80)^2 + 59(85)^2 + 50(90)^2 + 10(95)^2 + 2(100)^2 \end{matrix} \right\}^{1/2} \mathrm{km\,h^{-1}} = \boxed{86.4\ \mathrm{km\,h^{-1}}}$$

This demonstrates that as always $\langle X^2 \rangle^{1/2} > \langle X \rangle$ for observable X.

P20.4 $\kappa = \tfrac{1}{3}\lambda \bar{c} C_{V,\mathrm{m}}[\mathrm{A}]\,[20.23]$ and $\bar{c} = \left(\dfrac{8RT}{\pi M}\right)^{1/2}\,[20.7] \propto T^{1/2}$

Hence, $\kappa \propto T^{1/2} C_{V,\mathrm{m}}$ and $\dfrac{\kappa'}{\kappa} = \left(\dfrac{T'}{T}\right)^{1/2} \times \left(\dfrac{C'_{V,\mathrm{m}}}{C_{V,\mathrm{m}}}\right)$

The molar heat capacities at the two temperatures are estimated with the equipartition theorem. At 300 K there are three translational degrees of freedom and two rotational degrees of freedom, which gives $C_{V,\mathrm{m}} \approx (3+2)\frac{1}{2}R = \frac{5}{2}R$. At 10 K the rotational degrees of freedom are not significantly populated so there are three translational degrees of freedom alone, which gives $C_{V,\mathrm{m}} \approx \frac{3}{2}R$.

Therefore, $\dfrac{\kappa'}{\kappa} = \left(\dfrac{300}{10}\right)^{1/2} \times \left(\dfrac{5}{3}\right) = \boxed{9.1}$

P20.6 The atomic current is the number of atoms emerging from the slit per second, which is $Z_\mathrm{W}A$ with $A = 1.0 \times 10^{-7}\ \mathrm{m}^2$. We use

$$Z_\mathrm{W} = \frac{p}{(2\pi mkT)^{1/2}}\ [20.14]$$

$$= \frac{p/\mathrm{Pa}}{[(2\pi) \times (M/\mathrm{g\ mol^{-1}}) \times (1.6605 \times 10^{-27}\ \mathrm{kg}) \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (380\ \mathrm{K})]^{1/2}}$$

$$= (1.35 \times 10^{23}\ \mathrm{m^{-2}\ s^{-1}}) \times \left(\frac{p/\mathrm{Pa}}{(M/\mathrm{g\ mol^{-1}})^{1/2}}\right)$$

(a) Cadmium: $Z_\mathrm{W}A = (1.35 \times 10^{23}\ \mathrm{m^{-2}\ s^{-1}}) \times (1.0 \times 10^{-7}\ \mathrm{m}^2) \times \left(\dfrac{0.13}{(112.4)^{1/2}}\right) = \boxed{1.7 \times 10^{14}\ \mathrm{s^{-1}}}$

(b) Mercury: $Z_\mathrm{W}A = (1.35 \times 10^{23}\ \mathrm{m^{-2}\ s^{-1}}) \times (1.0 \times 10^{-7}\ \mathrm{m}^2) \times \left(\dfrac{12}{(200.6)^{1/2}}\right) = \boxed{1.1 \times 10^{16}\ \mathrm{s^{-1}}}$

P20.8 The molar conductivity, Λ_m, is related to the conductivity, κ, by $\Lambda_\mathrm{m} = \kappa/c$ [20.27] $= C/Rc$, where the cell constant is $C = 0.2063\ \mathrm{cm^{-1}}$. The **Kohlrausch law** [18.29] indicates that molar conductivity is linear in $c^{1/2}$.

$$\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\circ - \mathcal{K}c^{1/2}\ [20.28]$$

We draw a data table and calculate values for a plot of Λ_m against $c^{1/2}$.

$c/(\mathrm{mol\ dm^{-3}})$	0.00050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14
$c^{1/2}/(\mathrm{mol\ dm^{-3}})^{1/2}$	0.0224	0.0316	0.0707	0.100	0.141	0.224
$\Lambda_\mathrm{m}/(\mathrm{mS\ m^2\ mol^{-1}})$	12.45	12.36	12.06	11.85	11.58	11.11

The plot, shown in Figure 20.1, is linear and the linear regression fit yields the intercept and slope. The intercept is the limiting molar conductivity and the slope is the negative of the Kohlrausch parameter $\mathcal{K}$:

$$\Lambda_\mathrm{m}^\circ = \boxed{12.6\ \mathrm{mS\ m^2\ mol^{-1}}}$$

$$\mathcal{K} = \boxed{6.66\ \mathrm{mS\ m^2\ (mol\ dm^{-1})^{-3/2}}}$$

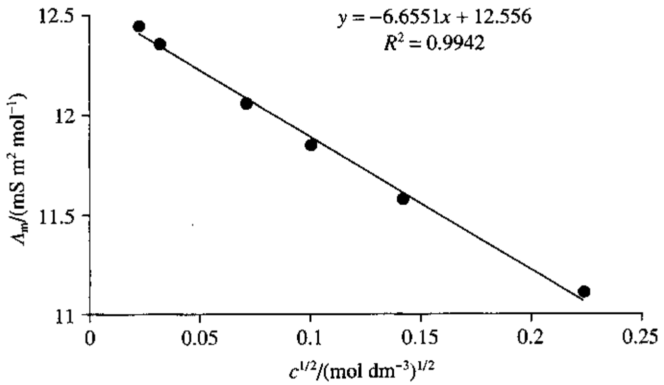


Figure 20.1

(a) $\Lambda_m = ((5.01 + 7.68) - 6.66 \times (0.010)^{1/2})\text{ mS m}^2\text{ mol}^{-1} = \boxed{12.02\text{ mS m}^2\text{ mol}^{-1}}$

(b) $\kappa = c\Lambda_m = (10\text{ mol m}^{-3}) \times (12.02\text{ mS m}^2\text{ mol}^{-1}) = 120\text{ mS m}^2\text{ m}^{-3} = \boxed{120\text{ mS m}^{-1}}$

(c) $R = \dfrac{C}{\kappa} = \dfrac{20.63\text{ m}^{-1}}{120\text{ mS m}^{-1}} = \boxed{172\ \Omega}$

P20.10 $s = u\mathcal{E}$ [20.34] with $\mathcal{E} = \dfrac{\Delta\varphi}{l}$ [20.30] $= \dfrac{10\text{ V}}{1.00\text{ cm}} = 10.0\text{ V cm}^{-1}$

Table 20.5 provides the ion mobilities, u.

$$s(\text{Li}^+) = (4.01 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}\text{ V}^{-1}) \times (10.0\text{ V cm}^{-1}) = \boxed{40.1\ \mu\text{m s}^{-1}}$$

$$s(\text{Na}^+) = (5.19 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}\text{ V}^{-1}) \times (10.0\text{ V cm}^{-1}) = \boxed{51.9\ \mu\text{m s}^{-1}}$$

$$s(\text{K}^+) = (7.62 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}\text{ V}^{-1}) \times (10.0\text{ V cm}^{-1}) = \boxed{76.2\ \mu\text{m s}^{-1}}$$

The drift speed equals the distance travelled in time t divided by t so 1.00 cm travel requires the times

$$t(\text{Li}^+) = \frac{1.0 \times 10^4\ \mu\text{m}}{40.1\ \mu\text{m s}^{-1}} = \boxed{249\text{ s}},\ t(\text{Na}^+) = \boxed{193\text{ s}},\text{ and } t(\text{K}^+) = \boxed{131\text{ s}}$$

(a) For the distance moved during a half-cycle, write

$$d = \int_0^{\nu/2} s\,dt = \int_0^{\nu/2} u\mathcal{E}\,dt = u\mathcal{E}_0 \int_0^{\nu/2} \sin(2\pi\nu t)dt \quad [\mathcal{E} = \mathcal{E}_0 \sin(2\pi\nu t)]$$

$$= \frac{u\mathcal{E}_0}{\pi\nu} = \frac{u \times (10.0\text{ V cm}^{-1})}{\pi \times (1.0 \times 10^3\text{ s}^{-1})}\text{[assume } \mathcal{E}_0 = 10\text{ V]} = (3.18 \times 10^{-3}\text{ V s cm}^{-1})u$$

That is, $d/\text{cm} = (3.18 \times 10^{-3}) \times (u/\text{cm}^2\text{ V}^{-1}\text{ s}^{-1})$. Hence,

$$d(\text{Li}^+) = (3.18 \times 10^{-3}) \times (4.01 \times 10^{-4})\text{ cm} = \boxed{12.8\text{ nm}}$$

$$d(\text{Na}^+) = (3.18 \times 10^{-3}) \times (5.19 \times 10^{-4})\text{ cm} = \boxed{16.5\text{ nm}}$$

$$d(\text{K}^+) = (3.18 \times 10^{-3}) \times (7.62 \times 10^{-4})\text{ cm} = \boxed{24.2\text{ nm}}$$

(b) These correspond to about $\boxed{43}$, $\boxed{55}$, and $\boxed{81}$ solvent molecule diameters, respectively.

P20.12 The linear gradation of colour indicates a constant concentration gradient across the length of the tube:

$$c = c_0 + \frac{\mathrm{d}c}{\mathrm{d}x}x,\ \text{where } c_0 = 0.100\ \text{mol dm}^{-3} \text{ is the concentration at } x = 0 \text{ and}$$

$$\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{\Delta c}{\Delta x} = \frac{(0.050 - 0.100)\ \text{mol dm}^{-3}}{10\ \text{cm}} = -5.0\times10^{-3}\ \text{mol dm}^{-3}\ \text{cm}^{-1} = -0.50\ \text{mol dm}^{-3}\ \text{m}^{-1}$$

Thus, the thermodynamic force is given by

$$\mathcal{F}(x) = -\frac{RT}{c}\frac{\mathrm{d}c}{\mathrm{d}x}\ [20.45]$$

$$= -\frac{(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})\times(298\ \text{K})}{0.100 - 0.0050\times(x/\text{cm})}\times(-0.50\ \text{m}^{-1})$$

$$= \frac{1.2\bar{4}\ \text{kN mol}^{-1}}{0.100 - 0.0050\times(x/\text{cm})}$$

(a) At $x = 0$, $\mathcal{F} = \boxed{12\ \text{kN mol}^{-1}} = 2.1\times10^{-20}$ N per molecule $= \boxed{21\ \text{zN per molecule}}$

(b) At $x = 5$ cm, $\mathcal{F} = \boxed{17\ \text{kN mol}^{-1}} = 2.7\times10^{-20}$ N per molecule $= \boxed{27\ \text{zN per molecule}}$

(c) At $x = 10$ cm, $\mathcal{F} = \boxed{25\ \text{kN mol}^{-1}} = 4.1\times10^{-20}$ N per molecule $= \boxed{41\ \text{zN per molecule}}$

P20.14 Since $D \propto \eta^{-1}$ [20.52] and $\eta \propto \mathrm{e}^{E_\mathrm{a}/RT}$ [20.25], we expect that $D \propto \mathrm{e}^{-E_\mathrm{a}/RT}$.

Therefore, if the diffusion constant is D at T and D' at T',

$$E_\mathrm{a} = -\frac{R\ln(D'/D)}{\left(\frac{1}{T'} - \frac{1}{T}\right)} = -\frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times\ln(2.89/2.05)}{\frac{1}{298\ \text{K}} - \frac{1}{273\ \text{K}}} = 9.3\ \text{kJ mol}^{-1}$$

That is, the activation energy for diffusion is $\boxed{9.3\ \text{kJ mol}^{-1}}$.

P20.16 $\langle x^2\rangle = 2Dt$ [20.60], $D = \dfrac{kT}{6\pi\eta a}$ [20.52]

$$\eta = \frac{kT}{6\pi Da} = \frac{kTt}{3\pi a\langle x^2\rangle} = \frac{(1.381\times10^{-23}\ \text{J K}^{-1})\times(298.15\ \text{K})\times t}{(3\pi)\times(2.12\times10^{-7}\ \text{m})\times\langle x^2\rangle}$$

$$= (2.06\times10^{-15}\ \text{J m}^{-1})\times\left(\frac{t}{\langle x^2\rangle}\right)$$

$$= (2.06\times10^{-3}\ \text{J m}^{-3}\ \text{s})\times\left(\frac{t/\text{s}}{\langle x^2\rangle/10^{-12}\ \text{m}^2}\right)$$

$$= (2.06\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1})\times\left(\frac{t/\text{s}}{\langle x^2\rangle/10^{-12}\ \text{m}^2}\right)$$

We draw up the following table:

t/s	30	60	90	120
$\langle x^2\rangle/10^{-12}\,\mathrm{m}^2$	88.2	113.5	128	144
$\eta/10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$	0.701	1.09	1.45	1.72

Hence, the mean value is $\boxed{1.2\times10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}}$.

P20.18 The viscosity of a perfect gas is

$$\eta=\frac{\frac{1}{3}M\lambda\bar{c}p}{N_AkT}\ [20.74\text{ with }[\mathrm{A}]=p/RT=p/N_AkT]$$

$$=\left(\frac{\frac{1}{3}Mp}{N_AkT}\right)\times\left(\frac{kT}{2^{1/2}\sigma p}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}$$

[Exercise 20.2(b) note, 20.7], where $\sigma=\pi d^2$ is the collision cross-section

$$=\left(\frac{2}{3\pi d^2N_A}\right)\times\left(\frac{MRT}{\pi}\right)^{1/2}$$

$$=\frac{2}{3d^2N_A}\left(\frac{MRT}{\pi^3}\right)^{1/2}.$$

$$\text{So, } d=\left\{\frac{2}{3\eta N_A}\left(\frac{MRT}{\pi^3}\right)^{1/2}\right\}^{1/2}$$

$$d=\left[\frac{2}{3\times(6.022\times10^{23}\,\mathrm{mol^{-1}})}\left\{\frac{(17.03\times10^{-3}\,\mathrm{kg\,mol^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{\pi^3}\right\}^{1/2}\times\frac{T^{1/2}}{\eta}\right]^{1/2}$$

$$\times\left(\frac{1\,\mathrm{pm}}{10^{-12}\,\mathrm{m}}\right)$$

$$=0.274\times\left\{\frac{(T/\mathrm{K})^{1/2}}{(\eta/\mathrm{kg\,m^{-1}\,s^{-1}})}\right\}^{1/2}\mathrm{pm}$$

(a) $d=0.274\times\left\{\frac{(270)^{1/2}}{(9.08\times10^{-6})}\right\}^{1/2}\mathrm{pm}=\boxed{369\,\mathrm{pm}}$

(b) $d=0.274\times\left\{\frac{(490)^{1/2}}{(1.749\times10^{-5})}\right\}^{1/2}\mathrm{pm}=\boxed{308\,\mathrm{pm}}$

COMMENT. The change in diameter with temperature can be interpreted in two ways. First, it shows the approximate nature of the concept of molecular diameter, with different values resulting from measurements of different quantities. Secondly, it is consistent with the idea that, at higher temperatures, more forceful collisions contract a molecule's perimeter.

Solutions to theoretical problems

P20.20 The most probable speed of a gas molecule corresponds to the condition that the Maxwell distribution be a maximum (it has no minimum), hence we find it by setting the first derivative of the function to zero and solving for the value of v at which this condition holds.

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \mathrm{e}^{-mv^2/2kT}\ [20.4] = \text{const} \times v^2\mathrm{e}^{-mv^2/2kT} \quad [M/R = m/k]$$

$$\frac{\mathrm{d}f(v)}{\mathrm{d}v} = 0, \quad \text{when}\left(2 - \frac{mv^2}{kT}\right) = 0.$$

$$\text{So, } \boxed{v(\text{most probable}) = c^* = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}}\ [20.8]$$

The average kinetic energy corresponds to the average of $\frac{1}{2}mv^2$. The average is obtained by determining

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\mathrm{d}v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \mathrm{e}^{-mv^2/2kT}\mathrm{d}v\ [20.4]$$

The integral evaluates to $\dfrac{3\pi^{1/2}}{8}\left(\dfrac{m}{2kT}\right)^{-5/2}$. Then, $\langle v^2 \rangle = 4\pi\left(\dfrac{m}{2\pi kT}\right)^{3/2} \times \dfrac{3\pi^{1/2}}{8}\left(\dfrac{m}{2kT}\right)^{-5/2} = \dfrac{3kT}{m}$

Thus, $\langle \varepsilon \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT$.

P20.22 Write the mean velocity initially as a; then in the emerging beam $\langle v_x \rangle = K\displaystyle\int_0^a v_x f(v_x)\mathrm{d}v_x$, where K is a constant that ensures that the distribution in the emergent beam is also normalized. That is,

$$1 = K\int_0^a f(v_x)\mathrm{d}v_x = K\left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^a \mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x$$

This integral cannot be evaluated analytically but it can be related to the error function by defining

$$\chi^2 = \frac{mv_x^2}{2kT}$$

which gives $\mathrm{d}v_x = \left(\dfrac{2kT}{m}\right)^{1/2}\mathrm{d}\chi$. Then,

$$1 = K\left(\frac{m}{2\pi kT}\right)^{1/2}\left(\frac{2kT}{m}\right)^{1/2}\int_0^b \mathrm{e}^{-\chi^2}\mathrm{d}\chi\ [b = (m/2kT)^{1/2} \times a] = \frac{K}{\pi^{1/2}}\int_0^b \mathrm{e}^{-\chi^2}\mathrm{d}\chi = \tfrac{1}{2}K\operatorname{erf}(b)$$

where erf (z) is the error function: $\operatorname{erf}(z) = (2/\pi^{1/2})\displaystyle\int_0^z \mathrm{e}^{-\chi^2}\mathrm{d}\chi$.

Therefore, $K = \dfrac{2}{\operatorname{erf}(b)}$.

The mean velocity of the emerging beam is

$$\langle v_x \rangle = K\left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^a v_x \mathrm{e}^{-mv_x^2/2kT} \mathrm{d}v_x$$

$$= K\left(\frac{m}{2\pi kT}\right)^{1/2} \left(\frac{-kT}{m}\right) \int_0^a \frac{\mathrm{d}}{\mathrm{d}v_x}(\mathrm{e}^{-mv_x^2/2kT} \mathrm{d}v_x)$$

$$= -K\left(\frac{kT}{2m\pi}\right)^{1/2} (\mathrm{e}^{-ma^2/2kT} - 1)$$

Now, use $a = \langle v_x \rangle_{\text{initial}} = (2kT/m\pi)^{1/2}$.

This expression for the average magnitude of the one-dimensional velocity in the x direction may be obtained from

$$\langle v_x \rangle_{\text{initial}} = 2\int_0^\infty v_x f(v_x) \mathrm{d}v_x = 2\int_0^\infty v_x \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT} \mathrm{d}v_x$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \left(\frac{2kT}{m}\right) = \left(\frac{2kT}{m\pi}\right)^{1/2}$$

It may also be obtained very quickly by setting $a = \infty$ in the expression for $\langle v_x \rangle$ in the emergent beam with $\operatorname{erf}(b) = \operatorname{erf}(\infty) = 1$.

Substituting $a = (2kT/\pi m)^{1/2}$ into $\langle v_x \rangle$ in the emergent beam, $\mathrm{e}^{-ma^2/2kT} = \mathrm{e}^{-1/\pi}$ and $\operatorname{erf}(b) = \operatorname{erf}(1/\pi^{1/2})$.

Therefore, $\langle v_x \rangle = \left(\dfrac{2kT}{m\pi}\right)^{1/2} \times \dfrac{1 - \mathrm{e}^{-1/\pi}}{\operatorname{erf}(1/\pi^{1/2})}$.

From tables of the error function, or from readily available software,

$$\operatorname{erf}(1/\pi^{1/2}) = \operatorname{erf}(0.56) = 0.57 \text{ and } \mathrm{e}^{-1/\pi} = 0.73$$

Therefore, $\langle v_x \rangle = \boxed{0.47\langle v_x \rangle_{\text{initial}}}$.

P20.24 The most probable speed, c^*, of a perfect gas is given by

$$c^* = \left(\frac{2kT}{m}\right)^{1/2} \quad \text{[20.8, derived in Problem 20.20]}$$

Consider a range of speeds Δv around c^* and nc^*, then

$$\frac{f(nc^*)}{f(c^*)} = \frac{(nc^*)^2 \mathrm{e}^{-mn^2c^{*2}/2kT}}{c^{*2}\ \mathrm{e}^{-mc^{*2}/2kT}} \text{[20.4]} = n^2\mathrm{e}^{-(n^2-1)mc^{*2}/2kT} = \boxed{n^2\mathrm{e}^{1-n^2}}$$

Therefore, $\dfrac{f(3c^*)}{f(c^*)} = 9 \times \mathrm{e}^{-8} = \boxed{3.02 \times 10^{-3}}$ and $\dfrac{f(4c^*)}{f(c^*)} = 16 \times \mathrm{e}^{-15} = \boxed{4.9 \times 10^{-6}}$

P20.26 The diffusion equation is: $\dfrac{\partial c}{\partial t} = D\dfrac{\partial^2 c}{\partial x^2}$ [20.53].

We confirm that $c(x,t) = \dfrac{a}{t^{1/2}}\mathrm{e}^{-bx^2/t}$ [20.57], where $a = \dfrac{n_0}{A(\pi D)^{1/2}}$ and $b = \dfrac{1}{4D}$, is a solution to the diffusion equation by taking both the partial derivative with respect to time and the second partial with respect to position to find whether or not they are proportional:

$$\frac{\partial c}{\partial t} = -\left(\frac{1}{2}\right)\times\left(\frac{a}{t^{3/2}}\right)\mathrm{e}^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right)\times\left(\frac{bx^2}{t^2}\right)\mathrm{e}^{-bx^2/t} = -\frac{c}{2t} + \frac{bx^2}{t^2}c$$

$$\frac{\partial c}{\partial x} = \left(\frac{a}{t^{1/2}}\right)\times\left(\frac{-2bx}{t}\right)\mathrm{e}^{-bx^2/t}$$

$$\frac{\partial^2 c}{\partial x^2} = -\left(\frac{2b}{t}\right)\times\left(\frac{a}{t^{1/2}}\right)\mathrm{e}^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right)\times\left(\frac{2bx}{t}\right)^2\mathrm{e}^{-bx^2/t} = -\left(\frac{2b}{t}\right)c + \left(\frac{2bx}{t}\right)^2 c$$

$$= -\left(\frac{1}{2Dt}\right)c + \left(\frac{bx^2}{Dt^2}\right)c = \frac{1}{D}\frac{\partial c}{\partial t} \text{ as required.}$$

Initially, the material is concentrated at $x = 0$. Note that $c = 0$ for $x > 0$ when $t = 0$ on account of the very strong exponential factor $\left(\mathrm{e}^{-bx^2t} \to 0 \text{ more strongly than } \dfrac{1}{t^{1/2}} \to \infty\right)$. When $x = 0$, $\mathrm{e}^{-x^2/4Dt} = 1$. We confirm the correct behaviour by noting that $\langle x\rangle = 0$ and $\langle x^2\rangle = 0$ at $t = 0$ [20.59 and 20.60], and so all the material must be at $x = 0$ at $t = 0$.

P20.28 The probability of being at x after time t is given by

$$P(x) = \left(\frac{2\tau}{\pi t}\right)^{1/2}\mathrm{e}^{-x^2\tau/2t\lambda^2} \text{ [20.61]}$$

$$P(6\lambda) = \left(\frac{2\tau}{\pi t}\right)^{1/2}\mathrm{e}^{-18\tau/t}$$

(a) After four steps: $t = 4\tau$

$$P(6\lambda) = \left(\frac{2\tau}{\pi\times(4\tau)}\right)^{1/2}\mathrm{e}^{-18\tau/(4\tau)} = \left(\frac{1}{2\pi}\right)^{1/2}\mathrm{e}^{-9/2} = 0.0043$$

The exact answer is $\boxed{\text{zero}}$ because the number of steps is insufficient to travel this distance.

(b) After six steps: $t = 6\tau$

$$P(6\lambda) = \left(\frac{2\tau}{\pi\times(6\tau)}\right)^{1/2}\mathrm{e}^{-18\tau/(6\tau)} = \left(\frac{1}{3\pi}\right)^{1/2}\mathrm{e}^{-3} = \boxed{0.0162}$$

(c) After 12 steps: $t = 12\tau$

$$P(6\lambda) = \left(\frac{2\tau}{\pi\times(12\tau)}\right)^{1/2}\mathrm{e}^{-18\tau/(12\tau)} = \left(\frac{1}{6\pi}\right)^{1/2}\mathrm{e}^{-3/2} = \boxed{0.0514}$$

Solutions to applications: astrophysics and biochemistry

P20.30 Newton's gravitational force law: $F = \dfrac{Gmm'}{r^2}$, where G is the gravitational constant and r is the centre-to-centre distance between mass m and m'. In this problem $r \geq R$, where R is a planet radius. The minimum work w required to move an object of mass m from a position near the planet's surface to infinity is

$$w = \int_R^\infty F\mathrm{d}r = Gmm'\int_R^\infty \frac{1}{r^2}\mathrm{d}r = -Gmm' \times \left[\frac{1}{r}\right]_{r=R}^{r=\infty} = \left(\frac{Gm'}{R}\right)m = mg_{\text{planet}}R$$

where $g_{\text{planet}} = \dfrac{Gm'}{R^2}$ is the gravitational acceleration of a planet and $\dfrac{g_{\text{planet}}}{g_{\text{Earth}}} = \left(\dfrac{m}{R^2}\right)_{\text{planet}} \Big/ \left(\dfrac{m}{R^2}\right)_{\text{Earth}}$.

Using data provided in the problem:

$$g_{\text{Mars}} = g_{\text{Earth}} \times \left(\frac{m}{R^2}\right)_{\text{Mars}} \Big/ \left(\frac{m}{R^2}\right)_{\text{Earth}} = g_{\text{Earth}} \times \left(\frac{m_{\text{Mars}}}{m_{\text{Earth}}}\right) \times \left(\frac{R_{\text{Earth}}}{R_{\text{Mars}}}\right)^2$$

$$= (9.81\ \text{m s}^{-2}) \times (0.108) \times \left(\frac{6.37}{3.38}\right)^2 = 3.76\ \text{m s}^{-2}$$

The escape speed v_{esc} is determined by the minimum kinetic energy that provides the energy w.

$$\tfrac{1}{2}mv_{\text{esc}}^2 = (gR)_{\text{planet}}m, \quad \text{so that} \quad v_{\text{esc}} = (2gR)_{\text{planet}}^{1/2}$$

(a) The escape speed for Earth: $v_{\text{esc}} = [2 \times (9.81\ \text{m s}^{-2}) \times (6.37 \times 10^6\ \text{m})]^{1/2} = \boxed{11.2\ \text{km s}^{-1}}$

(b) The escape speed for Mars: $v_{\text{esc}} = [2 \times (3.76\ \text{m s}^{-2}) \times (3.38 \times 10^6\ \text{m})]^{1/2} = \boxed{5.04\ \text{km s}^{-1}}$

Since $\bar{c} = (8RT/\pi M)^{1/2}$ [20.7], the temperature at which the mean gas speed corresponds to the escape speed is given by $T = \pi M v_{\text{esc}}^2/8R$ and computed temperature values for hydrogen, helium, and oxygen are summarized in the following table:

$10^{-3}T/K$	H_2	He	O_2	
Earth	11.9	23.7	190	[$\bar{c} = 11.2\ \text{km s}^{-1}$]
Mars	2.4	4.8	38	[$\bar{c} = 5.0\ \text{km s}^{-1}$]

In order to calculate the proportion P of molecules that have speeds exceeding the escape velocity, we must integrate the Maxwell distribution [20.4] from v_{esc} to infinity. P is a function of M, T, and v_{esc}:

$$P(M,T,v_{\text{esc}}) = \int_{v_{\text{esc}}}^\infty f(v)\mathrm{d}v = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_{v_{\text{esc}}}^\infty v^2 \mathrm{e}^{-Mv^2/2RT}\mathrm{d}v$$

The integral of this expression has no analytical solution but it is easily numerically performed on the scientific calculator or with computer software. Avoid unit errors by using SI units throughout. Here is a Mathcad setup for the computations along with the desired calculations:

$$R := 8.3145 \qquad P(M,T,v_{esc}) := 4\cdot\pi\cdot\left(\frac{M}{2\cdot\pi\cdot R\cdot T}\right)^{1.5}\cdot\int_{v_{esc}}^{\infty} v^2\cdot e^{\frac{-M\cdot v^2}{2\cdot R\cdot T}}\,dv$$

For gases of the Earth's atmosphere, $v_{esc} = 11.2 \times 10^3$ m s^{-1}:

Hydrogen at 240 K: $P(0.002016, 240, 11.2\cdot 10^3) = 2.498\times 10^{-27}$
Hydrogen at 1500 K: $P(0.002016, 1500, 11.2\cdot 10^3) = 1.487\times 10^{-4}$
Helium at 240 K: $P(0.004, 240, 11.2\cdot 10^3) = 3.210\times 10^{-54}$
Helium at 1500 K: $P(0.004, 1500, 11.2\cdot 10^3) = 9.516\times 10^{-9}$
Oxygen at 240 K: $P(0.032, 240, 11.2\cdot 10^3) = 0.000\times 10^{0}$
Oxygen at 1500 K: $P(0.032, 1500, 11.2\cdot 10^3) = 1.888\times 10^{-69}$

For gases of the Mars atmosphere, $v_{esc} = 5.04 \times 10^3$ m s^{-1}:

Hydrogen at 240 K: $P(0.002016, 240, 5.04\cdot 10^3) = 1.122\times 10^{-5}$
Hydrogen at 1500 K: $P(0.002016, 1500, 5.04\cdot 10^3) = 2.502\times 10^{-1}$
Helium at 240 K: $P(0.004, 240, 5.04\cdot 10^3) = 5.093\times 10^{-11}$
Helium at 1500 K: $P(0.004, 1500, 5.04\cdot 10^3) = 4.307\times 10^{-2}$
Oxygen at 240 K: $P(0.032, 240, 5.04\cdot 10^3) = 5.659\times 10^{-88}$
Oxygen at 1500 K: $P(0.032, 1500, 5.04\cdot 10^3) = 4.246\times 10^{-14}$

Based on these numbers alone, it would appear that H_2 and He would be depleted from the atmosphere of both Earth and Mars only after many (millions?) years, that the rate on Mars, although still slow, would be many orders of magnitude larger than on Earth, that O_2 would be retained on Earth indefinitely, and that the rate of O_2 depletion on Mars would be very slow (billions of years?), although not totally negligible. The temperatures of both planets may have been higher in past times than they are now.

P20.32 Dry atmospheric air is 78.08% N_2, 20.95% O_2, 0.93% Ar, and 0.03% CO_2, plus traces of other gases. Nitrogen, oxygen, and carbon dioxide contribute 99.06% of the molecules in a volume with each molecule contributing an average rotational energy equal to kT. The rotational energy density is given by

$$\rho_R = \frac{E_R}{V} = \frac{0.9906N\langle\varepsilon^R\rangle}{V} = \frac{0.9906\langle\varepsilon^R\rangle pN_A}{RT} = \frac{0.9906\,kTpN_A}{RT}$$
$$= 0.9906p = 0.9906(1.013\times 10^5\ \text{Pa}) = 0.1004\ \text{J cm}^{-3}$$

The total energy density (translational plus rotational) is

$$\rho_T = \rho_K + \rho_R = 0.15\ \text{J cm}^{-3} + 0.10\ \text{J cm}^{-3} = \boxed{0.25\ \text{J cm}^{-3}}$$

P20.34 For order of magnitude calculations we restrict our assumed values to powers of 10 of the base units. Thus,

$\rho = 1$ g cm^{-3} $= 1\times 10^3$ kg m^{-3}
$\eta(\text{air}) = 1\times 10^{-5}$ kg m^{-1} s^{-1} [see comment and question below]

We need the diffusion constant:

$$D = \frac{kT}{6\pi\eta a}$$

a is calculated from the volume of the virus, which is assumed to be spherical:

$$V = \frac{m}{\rho} \approx \frac{(1\times 10^{5}\, m_{\mathrm{u}})\times(1\times 10^{-27}\,\mathrm{kg}\, m_{\mathrm{u}}^{-1})}{1\times 10^{3}\,\mathrm{kg\,m^{3}}} \approx 1\times 10^{-25}\,\mathrm{m^{3}}$$

$$V = \tfrac{4}{3}\pi a^{3}$$

$$a \approx \left(\frac{V}{4}\right)^{1/3} \approx \left(\frac{1\times 10^{-25}\,\mathrm{m^{3}}}{4}\right)^{1/3} \approx 1\times 10^{-8}\,\mathrm{m}$$

$$D \approx \frac{(1\times 10^{-23}\,\mathrm{J\,K^{-1}})\times(300\,\mathrm{K})}{6\pi\times(1\times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}})\times(1\times 10^{-8}\,\mathrm{m})} \approx 1\times 10^{-9}\,\mathrm{m^{2}\,s^{-1}}$$

For three-dimensional diffusion:

$$t = \frac{\langle r^{2}\rangle}{6D} \approx \frac{1\,\mathrm{m^{2}}}{1\times 10^{-8}\,\mathrm{m^{2}\,s^{-1}}} \approx 10^{8}\,\mathrm{s} \approx \boxed{300\,\mathrm{y}}$$

Therefore, it does not seem likely that a cold could be caught by the process of diffusion.

COMMENT. In a Fermi calculation only those values of physical quantities that can be determined by scientific common sense should be used. Perhaps the value for η(air) used above does not fit that description.

Question. Can you obtain the value of η(air) by a Fermi calculation based on the relationship in Table 20.3?

P20.36 $c(x,t) = c_0 + (c_{\mathrm{s}} - c_0)\{1 - \operatorname{erf}(\xi)\}$, where $\xi(x,t) = x/(4Dt)^{1/2}$ and $\operatorname{erf}(\xi) = 1 - \dfrac{2}{\pi^{1/2}}\displaystyle\int_{\xi}^{\infty} e^{y^{2}}\,\mathrm{d}y$

In order for $c(x,t)$ to be the correct solution of this diffusion problem it must satisfy the boundary condition, the initial condition, and the diffusion equation [eqn 20.53]. At the boundary $x = 0$, $\xi = 0$, and $\operatorname{erf}(0) = 1 - \dfrac{2}{\pi^{1/2}}\displaystyle\int_{0}^{\infty} e^{-y^{2}}\mathrm{d}y = 1 - \left(\dfrac{2}{\pi^{1/2}}\right)\times\left(\dfrac{\pi^{1/2}}{2}\right) = 0.$

Thus, $c(0,t) = c_0 + (c_{\mathrm{s}} - c_0)\{1 - 0\} = c_{\mathrm{s}}$. The boundary condition is satisfied. At the initial time ($t = 0$), $\xi(x,0) = \infty$ and $\operatorname{erf}(\infty) = 1$. Thus, $c(x,0) = c_0 + (c_{\mathrm{s}} - c_0)\{1 - 1\} = c_0$. The initial condition is satisfied. We must find the analytical forms for $\partial c/\partial t$ and $\partial^{2}c/\partial x^{2}$. If they are proportional with a constant of proportionality equal to D, $c(x,t)$ satisfies the diffusion equation.

$$\frac{\partial c(x,t)}{\partial x} = D\left[\frac{1}{2}\frac{(c_{\mathrm{s}} - c_0)x}{\sqrt{\pi}(Dt)^{3/2}}\mathrm{e}^{-x^{2}/4Dt}\right]$$

$$\frac{\partial^{2} c(x,t)}{\partial x^{2}} = \left[\frac{1}{2}\frac{(c_{\mathrm{s}} - c_0)x}{\sqrt{\pi}(Dt)^{3/2}}\mathrm{e}^{-x^{2}/4Dt}\right]$$

The constant of proportionality between the partials equals D and we conclude that the suggested solution satisfies the diffusion equation.

Diffusion through alveoli sites (about 1 cell thick) of oxygen and carbon dioxide between lungs and blood capillaries (also about 1 cell thick) occurs through about 0.075 mm (the diameter of a red blood cell). So, we will examine diffusion profiles for $0 \le x \le 0.1$ mm. The largest distance suggests that the longest time that must be examined is estimated with eqn 20.59.

$$t_{\max} \approx \frac{\pi x_{\max}^2}{4D} = \frac{\pi(1\times10^{-4}\,\mathrm{m})^2}{4(2.10\times10^{-9}\,\mathrm{m^2\,s^{-1}})} = 3.74\,\mathrm{s}$$

Figure 20.2 shows oxygen concentration distributions for times between 0.01 s and 4.0 s. We set c_0 equal to zero and calculate c_s with Henry's law [Section 5.3(b), eqn 5.23].

$$b_{O_2} = \frac{p_{O_2}}{K_{O_2}}\ [16.26\mathrm{b\ and\ }\textit{Brief illustration}\mathrm{\ of\ Section\ 5.3b}] = \frac{21\,\mathrm{kPa}}{7.9\times10^4\,\mathrm{kPa\,kg\,mol^{-1}}}\ [\mathrm{Table\ 5.1}]$$
$$= 2.7\times10^{-4}\,\mathrm{mol\,kg^{-1}}$$

So, $c_s = 2.7\times10^{-4}\,\mathrm{mol\,dm^{-3}}$.

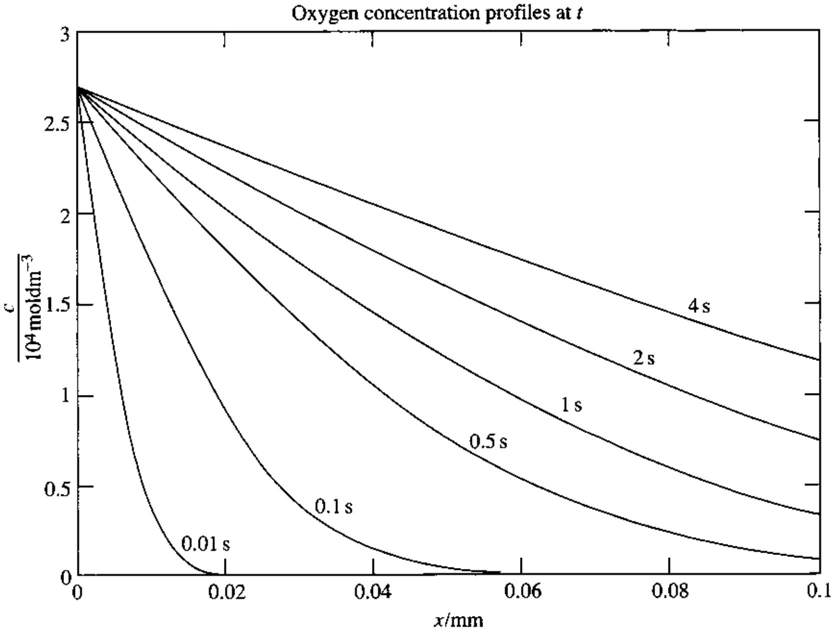


Figure 20.2

21

The rates of chemical reactions

Answers to discussion questions

D21.2 The determination of a rate law is simplified by the isolation method in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be $v = k_r[A][B]$, we can approximate [B] by $[B]_0$ and write

$$v = k_r'[A], \text{ where } k_r' = k_r[B]_0 \quad [21.10]$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, it is called a pseudo-first-order rate law. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing the overall rate law.

In the method of initial rates, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is $v = k_r[A]^a$; then its initial rate, v_0, is given by the initial values of the concentration of A, and we write $v_0 = k_r[A]_0^a$. Taking logarithms gives

$$\log v_0 = \log k_r + a \log [A]_0 \quad [21.11]$$

For a series of initial concentrations, a plot of the logarithms of the initial rates against the logarithms of the initial concentrations of A should be a straight line with slope a.

The method of initial rates might not reveal the full rate law, for the products may participate in the reaction and affect the rate. For example, products participate in the synthesis of HBr, where the full rate law depends on the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. The fitting may be done, in simple cases at least, by using a proposed rate law to predict the concentration of any component at any time, and comparing it with the data.

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions are easily obtained and prove to be very useful. These are summarized in Table 21.3. In order to determine the rate law, one plots the right-hand side of the integrated rate laws shown in the table against t in order to see which of them results in a straight line through the origin. The one that does is the correct rate law.

D21.4 The parameter A, which corresponds to the intercept of the line at $1/T = 0$ (at infinite temperature), is called the pre-exponential factor or the frequency factor. The parameter E_a, which is obtained from the slope of the line $(-E_a/R)$, is called the activation energy. Collectively, the two quantities are called the Arrhenius parameters.

The temperature dependence of some reactions is not Arrhenius-like, in the sense that a straight line is not obtained when $\ln k$ is plotted against $1/T$. However, it is still possible to define an activation energy as

$$E_a = RT^2\left(\frac{\mathrm{d}\ln k}{\mathrm{d}T}\right) \text{ [21.30]}$$

This definition reduces to the earlier one (as the slope of a straight line) for a temperature-independent activation energy. However, this latter definition is more general because it allows E_a to be obtained from the slope (at the temperature of interest) of a plot of $\ln k$ against $1/T$ even if the Arrhenius plot is not a straight line. Non-Arrhenius behaviour is sometimes a sign that quantum-mechanical tunnelling is playing a significant role in the reaction.

D21.6 The rate-determining step is not just the slowest step: it must be slow *and* be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be side-stepped. The rate-determining step is like a slow ferry crossing between two fast highways: the overall rate at which traffic can reach its destination is determined by the rate at which it can cross on the ferry.

If the first step in a mechanism is the slowest step with the highest activation energy, then it is rate determining, and the overall reaction rate is equal to the rate of the first step because all subsequent steps are so fast that once the first intermediate is formed it results immediately in the formation of products. Once over the initial barrier, the intermediates cascade into products. However, a rate-determining step may also stem from the low concentration of a crucial reactant or catalyst and need not correspond to the step with highest activation barrier. A rate-determining step arising from the low activity of a crucial enzyme can sometimes be identified by determining whether or not the reactants and products for that step are in equilibrium: if the reaction is not at equilibrium it suggests that the step may be slow enough to be rate-determining.

D21.8 In the analysis of stepwise polymerization, the rate constant for the second-order condensation is assumed to be independent of the chain length and to remain constant throughout the reaction. It follows, then, that the degree of polymerization is given by

$$\langle N\rangle = 1 + k_r t[\mathrm{A}]_0 \text{ [21.68b]}$$

Therefore, the average molar mass can be controlled by adjusting the initial concentration of monomer and the length of time that the polymerization is allowed to proceed.

Chain polymerization is a complicated radical chain mechanism involving initiation, propagation, and termination steps (see Section 21.9(b) for the details of this mechanism). The derivation of the overall rate equation utilizes the steady-state approximation and leads to the following expression for the average number of monomer units in the polymer chain:

$$\langle N\rangle = 2k_r[\mathrm{M}][\mathrm{I}]^{-1/2} \text{ [21.75]}$$

where $k_r = \frac{1}{2}k_p(fk_ik_t)^{-1/2}$, where k_p, k_i, and k_t are the rate constants for the propagation, initiation, and termination steps, respectively, and f is the fraction of radicals that successfully initiate a chain.

We see that the average molar mass of the polymer is directly proportional to the monomer concentration, and inversely proportional to the square root of the initiator concentration and to the rate constant for initiation, therefore the slower the initiation of the chain, the higher the average molar mass of the polymer.

D21.10 Both the Marcus theory of photo-induced electron transfer and the Förster theory of resonance energy transfer examine interactions between a molecule excited by absorption of electromagnetic energy (the chromophore S) and another molecule Q. They explain *different* mechanisms of quenching, that is, different ways that the chromophore gets rid of extra energy after absorbing a photon through intermolecular interactions. Another common feature of the two is that they depend on physical proximity of S and Q: they must be close for action to be efficient.

In the Marcus theory, the rate of electron transfer depends on the reaction Gibbs energy of electron transfer, $\Delta_r G$, and on the energy cost to S, Q, and the reaction medium of any concomitant molecular rearrangement. The rate is enhanced when the driving force ($\Delta_r G$) and the reorganization energy are well matched.

Resonant energy transfer in the Förster mechanism is most efficient when Q can directly absorb electromagnetic radiation from S. The oscillating dipole moment of S is induced by the electromagnetic radiation it absorbed. It transfers the excitation energy of the radiation to Q via a mechanism in which its oscillating dipole moment induces an oscillating dipole moment in Q. This energy transfer can be efficient when the absorption spectrum of the acceptor (Q) overlaps with the emission spectrum of the donor (S).

Solutions to exercises

E21.1(b) The initial amount of NH_3 is assumed to be zero. Let its final amount be n_{am}, and let α be the fraction of that final amount produced during any given time. Thus, α varies from 0 to 1 over the course of the reaction. At any given time, the amount of ammonia produced up to that time is αn_{am}, the amount of nitrogen consumed is $\alpha n_{am}/2$, and the amount of hydrogen consumed is $3\alpha n_{am}/2$. If we let $n_{initial}$ be the total quantity of gas initially present (H_2 and N_2), then the total at any given time will be

$$n_{total} = n_{initial} - \alpha n_{am}/2 - 3\alpha n_{am}/2 + \alpha n_{am} = n_{initial} - \alpha n_{am}$$

Thus, the total amount of gas changes from $n_{initial}$ to $n_{initial} - n_{am}$ over the course of the reaction. (Note that total gas amount decreases at the same rate as ammonia is produced.) Since the volume and temperature do not change, we may also write

$$\boxed{p_{total} = p_{initial} - \alpha p_{am}}$$

E21.2(b) $$v = \frac{1}{\nu_J}\frac{d[J]}{dt} \text{ [21.3b]}, \quad \text{so} \quad \frac{d[J]}{dt} = \nu_J v$$

Rate of consumption of A $= v = \boxed{2.7\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

Rate of consumption of B $= 3v = \boxed{8.1\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

Rate of formation of C $= v = \boxed{2.7\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

Rate of formation of D $= 2v = \boxed{5.4\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

E21.3(b) $$v = \frac{1}{\nu_J}\frac{d[J]}{dt}\,[21.3b] = \frac{1}{3}\frac{d[B]}{dt} = \tfrac{1}{3} \times (2.7\ \text{mol dm}^{-3}\,\text{s}^{-1}) = \boxed{0.9\ \text{mol dm}^{-3}\,\text{s}^{-1}}$$

Rate of formation of C $= v = \boxed{0.9\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

Rate of formation of D $= 2v = \boxed{1.8\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

Rate of consumption of A $= v = \boxed{0.9\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

Rate of consumption of B $= 3v = \boxed{2.7\ \text{mol dm}^{-3}\,\text{s}^{-1}}$

E21.4(b) The rate is expressed in mol dm^{-3} s^{-1}, therefore

$$\text{mol dm}^{-3}\,\text{s}^{-1} = [k_r] \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^2$$

where $[k_r]$ denotes units of k_r, requires the units to be $\boxed{\text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1}}$

(a) Rate of consumption of A $= v = \boxed{k_r[A][B]^2}$

(b) Rate of formation of C $= v = \boxed{k_r[A][B]^2}$

E21.5(b) Given $\dfrac{d[C]}{dt} = k_r[A][B][C]^{-1}$

the rate of reaction is [21.3b]

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt} = \frac{d[C]}{dt} = \boxed{k_r[A][B][C]^{-1}}$$

The units of k_r, $[k_r]$, must satisfy

$$\text{mol dm}^{-3}\,\text{s}^{-1} = [k_r] \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^{-1}$$

Therefore, $[k_r] = \boxed{\text{s}^{-1}}$

E21.6(b) (a) For a second-order reaction, denoting the units of k_r by $[k_r]$

$$\text{molecule m}^{-3}\,\text{s}^{-1} = [k_r] \times (\text{molecule m}^{-3})^2\text{, therefore } [k_r] = \boxed{\text{m}^3\,\text{molecule}^{-1}\,\text{s}^{-1}} \text{ or } \boxed{\text{m}^3\,\text{s}^{-1}}$$

For a third-order reaction

$$\text{molecule m}^{-3}\,\text{s}^{-1} = [k_r] \times (\text{molecule m}^{-3})^3\text{, therefore } [k_r] = \boxed{\text{m}^6\,\text{molecule}^{-2}\,\text{s}^{-1}} \text{ or } \boxed{\text{m}^6\,\text{s}^{-1}}$$

COMMENT. Technically, 'molecule' is not a unit, so a number of molecules is simply a number of individual objects, that is, a pure number. In the chemical kinetics literature, it is common to see rate constants reported in molecular units of m^3 s^{-1}, m^6 s^{-1}, cm^3 s^{-1}, etc., with the number of molecules left unstated.

(b) For a second-order reaction

$$\text{Pa s}^{-1} = [k_r] \times \text{Pa}^2\text{, therefore } \boxed{[k_r] = \text{Pa}^{-1}\,\text{s}^{-1}}$$

For a third-order reaction

$$\text{Pa s}^{-1} = [k_r] \times \text{Pa}^3\text{, therefore } \boxed{[k_r] = \text{Pa}^{-2}\,\text{s}^{-1}}$$

E21.7(b) The rate law is

$$v = k_r[\mathrm{A}]^a \propto p_\mathrm{A}^a = \{p_{\mathrm{A},0}(1-f)\}^a$$

where f is the fraction reacted. Thus,

$$\frac{v_1}{v_2} = \frac{p_{\mathrm{A},1}^a}{p_{\mathrm{A},2}^a} = \left(\frac{1-f_1}{1-f_2}\right)^a$$

Taking logarithms

$$\ln\left(\frac{v_1}{v_2}\right) = a\ln\left(\frac{1-f_1}{1-f_2}\right)$$

$$\text{so}\quad a = \frac{\ln\left(\dfrac{v_1}{v_2}\right)}{\ln\left(\dfrac{1-f_1}{1-f_2}\right)} = \frac{\ln\left(\dfrac{9.71}{7.67}\right)}{\ln\left(\dfrac{0.90}{0.80}\right)} = 2.0$$

The reaction is $\boxed{\text{second order}}$.

COMMENT. Knowledge of the initial pressure is not required for the solution to this exercise. The ratio of pressures was computed using fractions of the initial pressure.

E21.8(b) Table 21.3 gives a general expression for the half-life of a reaction of the type A → P for orders other than 1:

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k_r[\mathrm{A}]_0^{n-1}} \propto [\mathrm{A}]_0^{1-n} \propto p_0^{1-n}$$

Form a ratio of the half-lives at different initial pressures:

$$\frac{t_{1/2}(p_{0,1})}{t_{1/2}(p_{0,2})} = \left(\frac{p_{0,1}}{p_{0,2}}\right)^{1-n} = \left(\frac{p_{0,2}}{p_{0,1}}\right)^{n-1}$$

$$\text{Hence, } \ln\left(\frac{t_{1/2}(p_{0,1})}{t_{1/2}(p_{0,2})}\right) = (n-1)\ln\left(\frac{p_{0,2}}{p_{0,1}}\right)$$

$$\text{or}\quad (n-1) = \frac{\ln\left(\dfrac{340\ \mathrm{s}}{178\ \mathrm{s}}\right)}{\ln\left(\dfrac{28.9\ \mathrm{kPa}}{55.5\ \mathrm{kPa}}\right)} = -0.992 \approx -1$$

Therefore, $\boxed{n = 0.}$

E21.9(b) The rate law is

$$v = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_r[\mathrm{A}]$$

The half-life formula in eqn. 21.13 is based on the assumption that

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=k_{\mathrm{r}}[\mathrm{A}]$$

That is, it would be accurate to take the half-life from the table and say

$$t_{1/2}=\frac{\ln 2}{k_{\mathrm{r}}'}$$

where $k_{\mathrm{r}}'=2k_{\mathrm{r}}$. Thus,

$$\begin{aligned} t_{1/2}&=\frac{\ln 2}{2(3.56\times10^{-7}\,\mathrm{s}^{-1})}\\ &=\boxed{9.74\times10^{5}\,\mathrm{s}} \end{aligned}$$

Likewise, we modify the integrated rate law [eqn. 21.12(b)], noting that pressure is proportional to concentration:

$$p=p_0\mathrm{e}^{-2k_{\mathrm{r}}t}$$

(a) Therefore, after 50 s, we have

$$p=(33.0\ \mathrm{kPa})\mathrm{e}^{-2\times(3.56\times10^{-7}\,\mathrm{s}^{-1})\times(50\,\mathrm{s})}=\boxed{32.9\overline{99}\ \mathrm{kPa}}$$

(b) After 20 min,

$$p=(33.0\ \mathrm{kPa})\mathrm{e}^{-2\times(3.56\times10^{-7}\,\mathrm{s}^{-1})\times(20\times60\,\mathrm{s})}=\boxed{32.9\overline{7}\ \mathrm{kPa}}$$

E21.10(b) From Table 21.3, we see that for A + 2B → P the integrated second-order rate law is

$$k_{\mathrm{r}}t=\frac{1}{[\mathrm{B}]_0-2[\mathrm{A}]_0}\ln\left[\frac{[\mathrm{A}]_0([\mathrm{B}]_0-2[\mathrm{P}])}{([\mathrm{A}]_0-[\mathrm{P}])[\mathrm{B}]_0}\right]$$

By the time [B] falls to 0.010 mol dm^{-3}, it has dropped by 0.020 mol dm^{-3}, so the [A] has fallen by 0.010 mol dm^{-3} to 0.040 mol dm^{-3}, and the [P] has risen by 0.010 mol dm^{-3} to 0.010 mol dm^{-3}.

(a) Substituting the data after solving for k_{r}

$$\begin{aligned} k_{\mathrm{r}}&=\frac{1}{(3.6\times10^{3}\,\mathrm{s})\times(0.030-2\times0.050)\ \mathrm{mol\ dm^{-3}}}\times\ln\left[\frac{0.050\times(0.030-2\times0.010)}{(0.050-0.010)\times0.030}\right]\\ &=\boxed{3.5\times10^{-3}\,\mathrm{dm^{3}\,mol^{-1}\,s^{-1}}} \end{aligned}$$

(b) The half-life in terms of A is the time when $[\mathrm{A}]=[\mathrm{A}]_0/2=0.025$ mol dm^{-3}. The stoichiometry requires [B] to drop by 0.050 mol dm^{-3}; however, since $[\mathrm{B}]_0$ was only 0.030 mol dm^{-3}, this concentration cannot be reached from the given initial conditions. The half-life of A, then, is $\boxed{\text{infinite}}$, since there is not enough B to react with it.

The half-life in terms of B is the time when $[\mathrm{B}]=[\mathrm{B}]_0/2=0.015$ mol dm^{-3}, $[\mathrm{A}]=[\mathrm{A}]_0-[\mathrm{B}]_0/4=$ 0.0425 mol dm^{-3}, and $[\mathrm{P}]=[\mathrm{B}]_0/4=0.0075$ mol dm^{-3}:

$$t_{1/2}(\mathrm{B}) = \frac{1}{k_\mathrm{r}([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} \ln\left[\frac{[\mathrm{A}]_0([\mathrm{B}]_0 - 2[\mathrm{P}])}{([\mathrm{A}]_0 - [\mathrm{P}])[\mathrm{B}]_0}\right]$$

$$= \frac{1}{(3.5 \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times (0.030 - 2 \times 0.050)\,\mathrm{mol\,dm^{-3}}} \times \ln\left(\frac{0.050 \times 0.015}{0.0425 \times 0.030}\right)$$

$$= \boxed{2.2 \times 10^3\,\mathrm{s}} = \boxed{0.61\,\mathrm{h}}$$

E21.11(b) The integrated rate law is

$$k_\mathrm{r}t = \frac{1}{[\mathrm{B}]_0 - 2[\mathrm{A}]_0} \ln\frac{[\mathrm{A}]_0([\mathrm{B}]_0 - 2[\mathrm{C}])}{([\mathrm{A}]_0 - [\mathrm{C}])[\mathrm{B}]_0} \text{ [Table 21.3]}$$

Solving for [C] yields, after some rearranging

$$[\mathrm{C}] = \frac{[\mathrm{A}]_0[\mathrm{B}]_0(\mathrm{e}^{k_\mathrm{r}t([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} - 1)}{[\mathrm{B}]_0\mathrm{e}^{k_\mathrm{r}t([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} - 2[\mathrm{A}]_0}$$

so $$\frac{[\mathrm{C}]}{\mathrm{mol\,dm^{-3}}} = \frac{(0.027) \times (0.130) \times (\mathrm{e}^{0.34 \times (0.130 - 2 \times 0.027) \times t/\mathrm{s}} - 1)}{(0.130) \times \mathrm{e}^{0.34 \times (0.130 - 2 \times 0.027) \times t/\mathrm{s}} - 2 \times (0.027)} = \frac{0.027 \times (\mathrm{e}^{0.026 \times t/\mathrm{s}} - 1)}{\mathrm{e}^{0.026 \times t/\mathrm{s}} - 0.42}$$

(a) $$[\mathrm{C}] = \frac{0.027 \times (\mathrm{e}^{0.026 \times 20} - 1)}{\mathrm{e}^{0.026 \times 20} - 0.42}\,\mathrm{mol\,dm^{-3}} = \boxed{0.014\,\mathrm{mol\,dm^{-3}}}$$

(b) $$[\mathrm{C}] = \frac{0.027 \times (\mathrm{e}^{0.026 \times 15 \times 60} - 1)}{\mathrm{e}^{0.026 \times 15 \times 60} - 0.42}\,\mathrm{mol\,dm^{-3}} = \boxed{0.027\,\mathrm{mol\,dm^{-3}}}$$

COMMENT. Note that part (b) tells us that the reaction is essentially complete after 15 min. In fact, it is essentially complete considerably before this time. When is the reaction 99% complete?

E21.12(b) The rate law is

$$v = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_\mathrm{r}[\mathrm{A}]^3$$

which integrates to

$$2k_\mathrm{r}t = \frac{1}{2}\left(\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_0^2}\right), \quad \text{so} \quad t = \frac{1}{4k_\mathrm{r}}\left(\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_0^2}\right)$$

$$t = \left(\frac{1}{4(6.50 \times 10^{-4}\,\mathrm{dm^6\,mol^{-2}\,s^{-1}})}\right) \times \left(\frac{1}{(0.015\,\mathrm{mol\,dm^{-3}})^2} - \frac{1}{(0.067\,\mathrm{mol\,dm^{-3}})^2}\right)$$

$$= \boxed{1.6 \times 10^6\,\mathrm{s}} = \boxed{19\text{ days}}$$

E21.13(b) The equilibrium constant of the reaction is the ratio of rate constants of the forward and reverse reactions:

$$K = \frac{k_\mathrm{r}}{k_\mathrm{r}'}, \quad \text{so} \quad k_\mathrm{r} = Kk_\mathrm{r}'$$

The relaxation time for the temperature jump is [Example 21.4]:

$$\tau = \{k_r + k_r'([\mathrm{B}]+[\mathrm{C}])\}^{-1}, \quad \text{so} \quad k_r = \tau^{-1} - k_r'([\mathrm{B}]+[\mathrm{C}])$$

Setting these two expressions for k_r equal yields

$$Kk_r' = \tau^{-1} - k_r'([\mathrm{B}]+[\mathrm{C}]), \quad \text{so} \quad k_r' = \frac{1}{\tau(K+[\mathrm{B}]+[\mathrm{C}])}$$

Hence,
$$k_r' = \frac{1}{(3.0\times10^{-6}\,\mathrm{s})\times(2.0\times10^{-16}+2.0\times10^{-4}+2.0\times10^{-4})\,\mathrm{mol\,dm^{-3}}}$$
$$= \boxed{8.3\times10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

and $k_r = (2.0\times10^{-16}\,\mathrm{mol\,dm^{-3}})\times(8.3\times10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = \boxed{1.7\times10^{-7}\,\mathrm{s^{-1}}}$

E21.14(b) The rate constant is given by

$$k_r = A\exp\left(\frac{-E_a}{RT}\right)\ [21.31]$$

so at 24°C it is

$$1.70\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}} = A\exp\left(\frac{-E_a}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times[(24+273)\,\mathrm{K}]}\right)$$

and at 37°C it is

$$2.01\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}} = A\exp\left(\frac{-E_a}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times[(37+273)\,\mathrm{K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70\times10^{-2}}{2.01\times10^{-2}} = \exp\left[\left(\frac{-E_a}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right)\times\left(\frac{1}{297\,\mathrm{K}}-\frac{1}{310\,\mathrm{K}}\right)\right]$$

so
$$\ln\left(\frac{1.70\times10^{-2}}{2.01\times10^{-2}}\right) = \left(\frac{-E_a}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right)\times\left(\frac{1}{297\,\mathrm{K}}-\frac{1}{310\,\mathrm{K}}\right)$$

and
$$E_a = -\left(\frac{1}{297\,\mathrm{K}}-\frac{1}{310\,\mathrm{K}}\right)^{-1}\ln\left(\frac{1.70\times10^{-2}}{2.01\times10^{-2}}\right)\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})$$
$$= 9.9\times10^{3}\,\mathrm{J\,mol^{-1}} = \boxed{9.9\,\mathrm{kJ\,mol^{-1}}}$$

With the activation energy in hand, the prefactor can be computed from either rate constant value

$$A = k_r\exp\left(\frac{E_a}{RT}\right) = (1.70\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})\times\exp\left(\frac{9.9\times10^{3}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(297\,\mathrm{K})}\right)$$
$$= \boxed{0.94\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

E21.15(b) Proceed as in Exercise 21.14(b):

$$E_a = \frac{R\ln\left(\dfrac{k_r(T_2)}{k_r(T_1)}\right)}{\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)} = \frac{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times\ln 2}{\dfrac{1}{298\ \mathrm{K}}-\dfrac{1}{308\ \mathrm{K}}} = \boxed{53\ \mathrm{kJ\,mol^{-1}}}$$

E21.16(b) Call the stable double helix S and the unstable one U. The rate of the overall reaction is

$$v = \frac{\mathrm{d[S]}}{\mathrm{d}t} = k_2[\mathrm{U}]$$

however, we cannot have the concentration of an intermediate in the overall rate law.

(i) Assume a pre-equilibrium with

$$K = \frac{[\mathrm{U}]}{[\mathrm{A}][\mathrm{B}]},\ \text{which implies } [\mathrm{U}] = K[\mathrm{A}][\mathrm{B}]$$

and $v = k_2[\mathrm{U}] = \boxed{k_2K[\mathrm{A}][\mathrm{B}]} = \boxed{k_{\mathrm{eff}}[\mathrm{A}][\mathrm{B}]}$ with $k_{\mathrm{eff}} = k_2K$

(ii) Apply the steady-state approximation:

$$\frac{\mathrm{d[U]}}{\mathrm{d}t} \approx 0 = k_1[\mathrm{A}][\mathrm{B}] - k_1'[\mathrm{U}] - k_2[\mathrm{U}]$$

so $[\mathrm{U}] = \dfrac{k_1[\mathrm{A}][\mathrm{B}]}{k_1'+k_2}$ and $v \approx \boxed{\dfrac{k_1k_2[\mathrm{A}][\mathrm{B}]}{k_1'+k_2}} = \boxed{k_{\mathrm{eff}}[\mathrm{A}][\mathrm{B}]}$ with $k_{\mathrm{eff}} = \dfrac{k_1k_2}{k_1'+k_2}$

COMMENT. The steady-state rate law reduces to the pre-equilibrium rate law if $k_1' \gg k_2$, which is likely to be the case if the first step is characterized as fast and the second slow. The steady-state approximation also encompasses the opposite possibility, that $k_1' \ll k_2$, in which case $k_{\mathrm{eff}} \approx k_1$, implying that the first step is rate limiting.

E21.17(b) $\dfrac{1}{k_r} = \dfrac{k_a'}{k_ak_b} + \dfrac{1}{k_ap_A}$ [analogous to 21.62]

Therefore, for two different pressures we have

$$\frac{1}{k_r(p_1)} - \frac{1}{k_r(p_2)} = \frac{1}{k_a}\left(\frac{1}{p_1}-\frac{1}{p_2}\right)$$

so $k_a = \left(\dfrac{1}{p_1}-\dfrac{1}{p_2}\right)\left(\dfrac{1}{k_r(p_1)}-\dfrac{1}{k_r(p_2)}\right)^{-1}$

$$= \left(\frac{1}{1.09\times10^3\ \mathrm{Pa}} - \frac{1}{25\ \mathrm{Pa}}\right)\times\left(\frac{1}{1.7\times10^{-3}\ \mathrm{s^{-1}}} - \frac{1}{2.2\times10^{-4}\ \mathrm{s^{-1}}}\right)^{-1}$$

$$= \boxed{9.9\times10^{-6}\ \mathrm{s^{-1}\,Pa^{-1}}} = \boxed{9.9\ \mathrm{s^{-1}\,MPa^{-1}}}.$$

E21.18(b) Let the steps be

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{I} \quad (\text{fast: } k_a,\ k_a')$$

and $\mathrm{I} \rightarrow \mathrm{P} \quad (k_b)$

Then, the rate of reaction is

$$v = \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_b[\mathrm{I}]$$

Applying the pre-equilibrium approximation yields

$$\frac{[\mathrm{I}]}{[\mathrm{A}][\mathrm{B}]} = K = \frac{k_a}{k_a'}, \quad \text{so} \quad [\mathrm{I}] = \frac{k_a[\mathrm{A}][\mathrm{B}]}{k_a'}$$

and $v = \dfrac{k_a k_b[\mathrm{A}][\mathrm{B}]}{k_a'} = k_r[\mathrm{A}][\mathrm{B}] \quad \text{with} \quad k_r = \dfrac{k_a k_b}{k_a'}$

Thus, $E_a = E_a(a) + E_a(b) - E_a'(a)\ [21.64] = (27 + 15 - 35)\ \mathrm{kJ\ mol^{-1}} = \boxed{7\ \mathrm{KJ\ mol^{-1}}}$

E21.19(b) The degree of polymerization is [21.68b]

$$\begin{aligned}\langle N\rangle &= 1 + k_r t[\mathrm{A}]_0 \\ &= 1 + (2.80 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}) \times 10.00\ \mathrm{h} \times 3600\ \mathrm{s\ h^{-1}} \times 5.00 \times 10^{-2}\ \mathrm{mol\ dm^{-3}} \\ &= \boxed{51.4}.\end{aligned}$$

The fraction condensed is related to the degree of polymerization by

$$\langle N\rangle = \frac{1}{1-p}, \quad \text{so} \quad p = \frac{\langle N\rangle - 1}{\langle N\rangle} = \frac{51.4 - 1}{51.4} = \boxed{0.981}$$

E21.20(b) The kinetic chain length varies with concentration as

$$\nu = k_r[\mathrm{M}][\mathrm{I}]^{-1/2}\ [21.74]$$

so the ratio of kinetic chain lengths under different concentrations is

$$\frac{\nu_2}{\nu_1} = \frac{[\mathrm{M}]_2}{[\mathrm{M}]_1} \times \left(\frac{[\mathrm{I}]_1}{[\mathrm{I}]_2}\right)^{1/2} = 5.0 \times (10.0)^{1/2} = \boxed{15.8}$$

E21.21(b) The quantum yield tells us that each mole of photons absorbed causes 1.2×10^2 moles of A to react [21.76a]; the stoichiometry tells us that 1 mole of B is formed for every mole of A that reacts. From the yield of 1.77 mmol B, we infer that 1.77 mmol A reacted, caused by the absorption of

$$\frac{(1.77 \times 10^{-3}\ \mathrm{mol}) \times (6.022 \times 10^{23}\ \mathrm{einstein^{-1}})}{1.2 \times 10^2\ \mathrm{mol\ einstein^{-1}}} = \boxed{4.4 \times 10^{18}}\ \text{photons}$$

E21.22(b) The quantum yield is defined as the amount of reacting molecules n_A divided by the amount of photons absorbed n_{abs}. The fraction of photons absorbed f_{abs} is one minus the fraction transmitted f_{trans}, and the amount of photons emitted n_{photon} can be inferred from the energy of the light source (power P times time t) and the energy of per photon (hc/λ).

$$\phi = \frac{n_A}{n_{abs}} = \frac{n_A hcN_A}{(1 - f_{trans})\lambda Pt}$$

$$= \frac{(0.324\ \text{mol}) \times (6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1}) \times (6.022 \times 10^{23}\ \text{mol}^{-1})}{(1 - 0.257) \times (320 \times 10^{-9}\ \text{m}) \times (87.5\ \text{W}) \times (28.0\ \text{min}) \times (60\ \text{s min}^{-1})}$$

$$= \boxed{1.11}.$$

E21.23(b) The Stern–Volmer equation [21.83] relates the ratio of fluorescence quantum yields in the absence and presence of quenching

$$\frac{\phi_{f,0}}{\phi_f} = 1 + \tau_0 k_Q[\text{Q}] = \frac{I_{f,0}}{I_f}$$

The last equality reflects the fact that fluorescence intensities are proportional to quantum yields. Solve this equation for [Q]:

$$[\text{Q}] = \frac{(I_{f,0}/I_f) - 1}{\tau_0 k_Q} = \frac{(100/75) - 1}{(3.5 \times 10^{-9}\text{s}) \times (2.5 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1})} = \boxed{0.038\ \text{mol dm}^{-3}}$$

E21.24(b) The efficiency of resonance energy transfer is given by [21.85]:

$$\eta_T = 1 - \frac{\phi_f}{\phi_{f,0}} = 0.15$$

Förster theory relates this quantity to the distance R between donor–acceptor pairs by

$$\eta_T = \frac{R_0^6}{R_0^6 + R^6}\ [21.86]$$

where R_0 is an empirical parameter listed in Table 21.7. Solving for the distance yields

$$R = R_0\left(\frac{1}{\eta_T} - 1\right)^{1/6} = (2.2\ \text{nm}) \times \left(\frac{1}{0.15} - 1\right)^{1/6} = \boxed{2.9\ \text{nm}}$$

Solutions to problems

Solutions to numerical problems

P21.2 A simple but practical approach is to make an initial guess at the order by observing whether the half-life of the reaction appears to depend on concentration. If it does not, the reaction is first order; otherwise refer to Table 21.3. Visual inspection of the data seems to indicate that the half-life is roughly independent of the concentration, therefore we first try to fit the data to eqn 21.12b:

$$\ln\left(\frac{[\text{A}]}{[\text{A}]_0}\right) = -k_r t$$

As in Example 21.3 we plot $\ln\left(\frac{[\text{A}]}{[\text{A}]_0}\right)$ against time to see if a straight line is obtained. We draw up the following table (A = $(\text{CH}_3)_3\text{CBr}$):

t/h	0	3.15	6.20	10.00	18.30	30.80
$[\text{A}]/(10^{-2}\ \text{mol dm}^{-3})$	10.39	8.96	7.76	6.39	3.53	2.07
$\dfrac{[\text{A}]}{[\text{A}]_0}$	1	0.862	0.747	0.615	0.340	0.199
$\ln\left(\dfrac{[\text{A}]}{[\text{A}]_0}\right)$	0	−0.148	−0.292	−0.486	−1.080	−1.613
$\left(\dfrac{1}{[\text{A}]}\right)/(\text{dm}^3\ \text{mol}^{-1})$	9.62	11.16	12.89	15.65	28.3	48.3

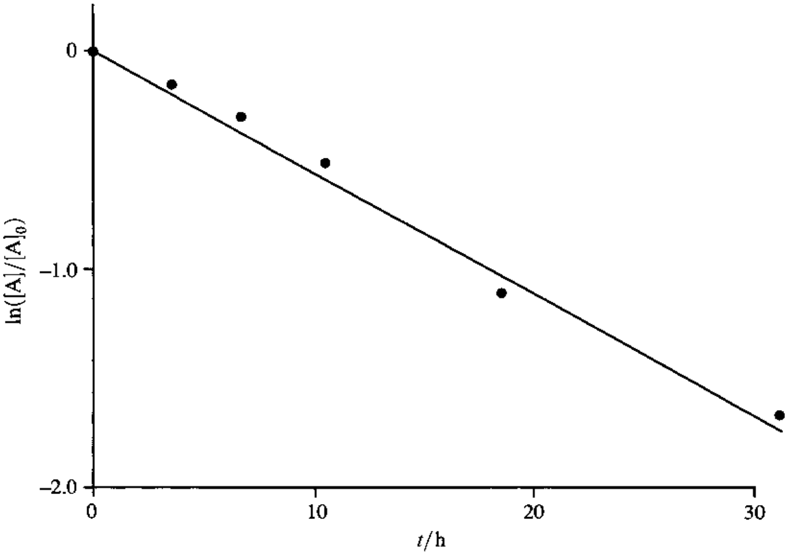


Figure 21.1

The data are plotted in Figure 21.1. The fit to a straight line is only fair, but the deviations look more like experimental scatter than systematic curvature. The correlation coefficient is 0.996. If we try to fit the data to the expression for a second-order reaction in Table 21.3, the fit is not as good; that correlation coefficient is 0.985. Thus, we conclude that the reaction is most likely $\boxed{\text{first order}}$. A non-integer order, neither first nor second, is also possible.

The rate constant k_r is the negative of the slope of the first-order plot:

$$k_r = 0.0542\ \text{h}^{-1} = \boxed{1.51\times10^{-5}\ \text{s}^{-1}}$$

At 43.8 h

$$\ln\left(\frac{[\text{A}]}{[\text{A}]_0}\right) = -(0.0542\ \text{h}^{-1})\times(43.8\ \text{h}) = -2.374$$

$$[\text{A}] = (10.39\times10^{-2}\ \text{mol dm}^{-3})\times e^{-2.359} = \boxed{9.67\times10^{-3}\ \text{mol dm}^{-3}}$$

P21.4 Examination of the data shows that the half-life remains constant at about 2 min. Therefore, the reaction is $\boxed{\text{first-order}}$. This can be confirmed by fitting any two pairs of data to the integrated first-order rate law, solving for the rate constant from each pair, and checking to see that they are the same to within experimental error:

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -k_r't \; [21.12\mathrm{b}, \mathrm{A} = \mathrm{N_2O_5}]$$

Note: k_r' is the rate constant in the differential equation

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_r'[\mathrm{A}]$$

Because of the stoichiometry of the reaction, the rate of the reaction is half the rate of consumption of N_2O_5:

$$v = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_r[\mathrm{A}] = \frac{k_r'}{2}[\mathrm{A}]$$

Solving for k_r',

$$k_r' = \frac{\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right)}{t}$$

At $t = 1.00$ min, $[\mathrm{A}] = 0.705$ mol dm^{-3} and

$$k_r' = \frac{\ln\left(\frac{1.000}{0.705}\right)}{1.00\ \mathrm{min}} = 0.350\ \mathrm{min}^{-1} = 5.83 \times 10^{-3}\ \mathrm{s}^{-1}$$

At $t = 3.00$ min, $[\mathrm{A}] = 0.349$ mol dm^{-3} and

$$k_r' = \frac{\ln\left(\frac{1.000}{0.349}\right)}{3.00\ \mathrm{min}} = 0.351\ \mathrm{min}^{-1} = 5.85 \times 10^{-3}\ \mathrm{s}^{-1}$$

Values of k_r' may be determined in a similar manner at all other times. The average value of k_r' obtained is $\boxed{5.84 \times 10^{-3}\ \mathrm{s}^{-1}}$ (which makes $\boxed{k_r = 2.92 \times 10^{-3}\ \mathrm{s}^{-1}}$). The constancy of k_r', which varies only between 5.83 and $5.85 \times 10^{-3}\ \mathrm{s}^{-1}$ confirms that the reaction is $\boxed{\text{first order}}$. A linear regression of ln[A] against t yields the same result. The half-life is [21.13]:

$$t_{1/2} = \frac{\ln 2}{k_r'} = \frac{0.693}{5.84 \times 10^{-3}\ \mathrm{s}^{-1}} = 118.\overline{7}\ \mathrm{s} = \boxed{1.98\ \mathrm{min}}.$$

P21.6 The data for this experiment do not extend much beyond one half-life. Therefore, the half-life method of predicting the order of the reaction as described in the solutions to Problems 21.1 and 21.2 cannot be used here. However, a similar method based on 'three-quarters lives' will work. For a first-order reaction, we may write (analogous to the derivation of eqn 21.13)

$$k_r t_{3/4} = -\ln\frac{\frac{3}{4}[A]_0}{[A]_0} = -\ln\frac{3}{4} = \ln\frac{4}{3} = 0.288 \quad \text{or} \quad t_{3/4} = \frac{0.288}{k_r}$$

Thus, the three-quarters life (or any given fractional life) is also independent of concentration for a first-order reaction. Examination of the data shows that the first three-quarters life (time to $[A] = 0.237\ \text{mol dm}^{-3}$) is about 80 min and by interpolation the second (time to $[A] = 0.178\ \text{mol dm}^{-3}$) is also about 80 min. Therefore, the reaction is first order and the rate constant is approximately

$$k_r = \frac{0.288}{t_{3/4}} \approx \frac{0.288}{80\ \text{min}} = 3.6 \times 10^{-3}\ \text{min}^{-1}$$

A least-squares fit of the data to the first-order integrated rate law [21.12b] gives the slightly more accurate result, $k_r = \boxed{3.65 \times 10^{-3}\ \text{min}^{-1}}$. The half-life is

$$t_{1/2} = \frac{\ln 2}{k_r} = \frac{\ln 2}{3.65 \times 10^{-3}\ \text{min}^{-1}} = \boxed{190\ \text{min}}$$

The average lifetime is calculated from

$$\frac{[A]}{[A]_0} = e^{-k_r t}\ [21.12b]$$

which has the form of a distribution function in the sense that the ratio $\frac{[A]}{[A]_0}$ is the fraction of sucrose molecules that have lived to time t. The average lifetime is then

$$\langle t \rangle = \frac{\int_0^\infty t e^{-k_r t}\,dt}{\int_0^\infty e^{-k_r t}\,dt} = \frac{1}{k_r} = \boxed{274\ \text{min}}$$

The denominator ensures normalization of the distribution function.

COMMENT. The average lifetime is also called the relaxation time. Note that the average lifetime is not the half-life. The latter is 190 min. Also note that $2 \times t_{3/4} \neq t_{1/2}$.

P21.8 The data do not extend much beyond one half-life, therefore we cannot see whether the half-life is constant over the course of the reaction as a preliminary step in guessing a reaction order. In a first-order reaction, however, not only the half-life but any other similarly defined fractional lifetime remains constant. (See Problem 21.6.) In this problem, we can see that the two-thirds-life is *not* constant. (It takes less than 1.6 ms for [ClO] to drop from the first recorded value ($8.49\ \mu\text{mol dm}^{-3}$) by more than a third of that value (to $5.79\ \mu\text{mol dm}^{-3}$); it takes more than 4.0 more ms for the concentration to drop by not even a third of *that* value (to $3.95\ \mu\text{mol dm}^{-3}$). So, our working assumption is that the reaction is not first order but second order. Draw up the following table:

The plot of 1/[ClO] vs. t (Figure 21.2) yields a reasonable straight line; the linear least-squares fit is:

$$(1/[\text{ClO}])/(\text{dm}^3\ \mu\text{mol}^{-1}) = 0.118 + 0.0237(t/\text{ms}) \qquad R^2 = 0.974$$

The rate constant is equal to the slope

$$k_r' = 0.0237\ \text{dm}^3\ \mu\text{mol}^{-1}\ \text{ms}^{-1} = \boxed{2.37 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

t/ms	[ClO]/(μmol dm^{-3})	(1/[ClO])/(dm^3 μmol^{-1})
0.12	8.49	0.118
0.62	8.09	0.124
0.96	7.10	0.141
1.60	5.79	0.173
3.20	5.20	0.192
4.00	4.77	0.210
5.75	3.95	0.253

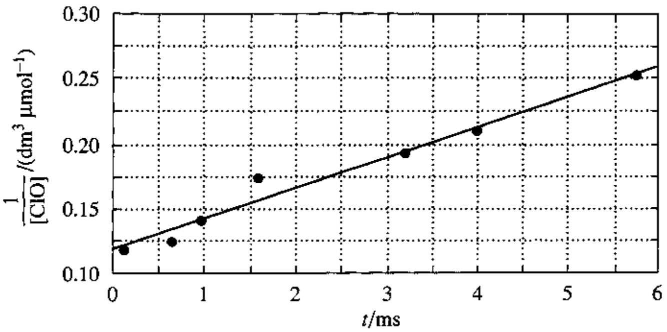


Figure 21.2

Note: k_r' is the rate constant in the differential equation

$$-\frac{d[\mathrm{ClO}]}{dt}=k_r'[\mathrm{ClO}]$$

Because of the stoichiometry of the reaction, the rate of the reaction is half the rate of consumption of ClO:

$$v=-\frac{1}{2}\frac{d[\mathrm{ClO}]}{dt}=k_r[\mathrm{ClO}]=\frac{k_r'}{2}[\mathrm{ClO}]$$

so $\boxed{k_r=1.18\times10^{7}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$

The half-life depends on the initial concentration [eqn 21.16]:

$$t_{1/2}=\frac{1}{k_r[\mathrm{ClO}]_0}=\frac{1}{(2.37\times10^{7}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})(8.47\times10^{-6}\,\mathrm{mol\,dm^{-3}})}=\boxed{4.98\times10^{-3}\,\mathrm{s}}$$

P21.10 $\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P},\quad \frac{d[\mathrm{P}]}{dt}=k_r[\mathrm{A}]^m[\mathrm{B}]^n$

and for a short interval δt,

$$\delta[\mathrm{P}]\approx k_r[\mathrm{A}]^m[\mathrm{B}]^n\delta t$$

Therefore, since $\delta[\mathrm{P}] = [\mathrm{P}]_t - [\mathrm{P}]_0 = [\mathrm{P}]_t$

$$\frac{[\mathrm{P}]}{[\mathrm{A}]} = k_r[\mathrm{A}]^{m-1}[\mathrm{B}]^n\delta t$$

$\dfrac{[\text{Chloropropane}]}{[\text{Propene}]}$ is independent of [Propene], implying that $m = 1$.

$$\frac{[\text{Chloropropane}]}{[\text{HCl}]} = \left\{\begin{array}{llll} p(\text{HCl}) & 10 & 7.5 & 5.0 \\ & 0.05 & 0.03 & 0.01 \end{array}\right.$$

These results suggest that the ratio is roughly proportional to $p(\text{HCl})^2$, and therefore that $m = 3$ when A is identified with HCl. The rate law is therefore

$$\frac{\mathrm{d}[\text{Chloropropane}]}{\mathrm{d}t} = k_r[\text{Propene}][\text{HCl}]^3$$

and the reaction is $\boxed{\text{first order}}$ in propene and $\boxed{\text{third order}}$ in HCl.

P21.12 If the rate constant obeys the Arrhenius equation [eqn 21.29], a plot of ln k against $1/T$ should yield a straight line with slope $-E_a/R$. Construct a table as follows:

k_r/s	θ/°C	10^3 K/T	ln k_r
2.46×10^{-3}	0	3.66	−6.01
0.0451	20	3.41	−3.10
0.576	40	3.19	−0.552

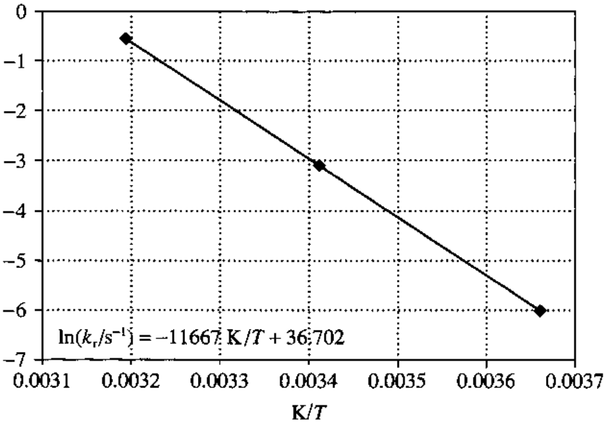


Figure 21.3

The plot is shown in Figure 21.3. The best-fit straight line fits the three data points very well:

$$\ln(k_r/\mathrm{s}^{-1}) = -1.17 \times 10^4\ \mathrm{K}/T + 36.7$$

so $E_a = -(-1.17 \times 10^4\ \mathrm{K}) \times (8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}) = \boxed{9.70 \times 10^4\ \mathrm{J\ mol^{-1}}} = \boxed{97.0\ \mathrm{kJ\ mol^{-1}}}$

P21.14 We can estimate the activation energy of the overall reaction by proceeding as in Exercise 21.14(a) and (b):

$$E_{\mathrm{a,eff}} = \frac{-R\ln\left(\frac{k_{\mathrm{eff}}}{k'_{\mathrm{eff}}}\right)}{\left(\frac{1}{T}-\frac{1}{T'}\right)} = \frac{-R\ln 3}{\frac{1}{292\ \mathrm{K}}-\frac{1}{343\ \mathrm{K}}} = \boxed{-18\ \mathrm{kJ\ mol^{-1}}}$$

To relate this quantity to the rate constants and equilibrium constants of the mechanism (Problem 21.11), we identify the effective rate constant as $k_{\mathrm{eff}} = kK_1K_2$ and apply the general definition of activation energy [eqn 21.30]:

$$E_{\mathrm{a,eff}} = RT^2\frac{\mathrm{d}\ln k_{\mathrm{eff}}}{\mathrm{d}T} = RT^2\frac{\mathrm{d}\ln k_{\mathrm{eff}}}{\mathrm{d}(1/T)}\frac{\mathrm{d}(1/T)}{\mathrm{d}T} = -R\frac{\mathrm{d}\ln k_{\mathrm{eff}}}{\mathrm{d}(1/T)}$$

This form is useful because rate constants and equilibrium constants are often more readily differentiated when considered as functions of $1/T$ rather than functions of T, as in this case:

$$\ln k_{\mathrm{eff}} = \ln k + \ln K_1 + \ln K_2$$

so $$E_{\mathrm{a,eff}} = -R\frac{\mathrm{d}\ln k_{\mathrm{eff}}}{\mathrm{d}(1/T)} = -R\frac{\mathrm{d}\ln k}{\mathrm{d}(1/T)} - R\frac{\mathrm{d}\ln K_1}{\mathrm{d}(1/T)} - R\frac{\mathrm{d}\ln K_2}{\mathrm{d}(1/T)} = E_{\mathrm{a}} + \Delta_{\mathrm{r}}H_1 + \Delta_{\mathrm{r}}H_2$$

since $\dfrac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \dfrac{-\Delta_{\mathrm{r}}H}{R}$ [van't Hoff equation, Section 6.4(a)]

Hence, $E_{\mathrm{a}} = E_{\mathrm{a,eff}} - \Delta_{\mathrm{r}}H_1 - \Delta_{\mathrm{r}}H_2 = (-18 + 14 + 14)\ \mathrm{kJ\ mol^{-1}} = \boxed{+10\ \mathrm{kJ\ mol^{-1}}}$

P21.16 (a) First, find an expression for the relaxation time, using Example 21.4 as a model:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -2k_{\mathrm{a}}[\mathrm{A}]^2 + 2k'_{\mathrm{a}}[\mathrm{A}_2]$$

Rewrite the expression in terms of a difference from equilibrium values, $[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + x$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}([\mathrm{A}]_{\mathrm{eq}}+x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t} = -2k_{\mathrm{a}}([\mathrm{A}]_{\mathrm{eq}}+x)^2 + 2k'_{\mathrm{a}}([\mathrm{A}_2]_{\mathrm{eq}} - \tfrac{1}{2}x)$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -2k_{\mathrm{a}}[\mathrm{A}]^2_{\mathrm{eq}} - 4k_{\mathrm{a}}[\mathrm{A}]_{\mathrm{eq}}x - 2k_{\mathrm{a}}x^2 + 2k'_{\mathrm{a}}[\mathrm{A}_2]_{\mathrm{eq}} - k'_{\mathrm{a}}x$$

Neglect powers of x greater than x^1, and use the fact that at equilibrium the forward and reverse rates are equal,

$$k_{\mathrm{a}}[\mathrm{A}]^2_{\mathrm{eq}} = k'_{\mathrm{a}}[\mathrm{A}_2]_{\mathrm{eq}}$$

to obtain

$$\frac{\mathrm{d}x}{\mathrm{d}t} \approx -(4k_{\mathrm{a}}[\mathrm{A}]_{\mathrm{eq}} + k'_{\mathrm{a}})x, \quad \text{so} \quad \frac{1}{\tau} \approx 4k_{\mathrm{a}}[\mathrm{A}]_{\mathrm{eq}} + k'_{\mathrm{a}}$$

To get the desired expression, square the reciprocal relaxation time,

(i) $$\frac{1}{\tau^2} \approx 16k_{\mathrm{a}}^2[\mathrm{A}]^2_{\mathrm{eq}} + 8k_{\mathrm{a}}k'_{\mathrm{a}}[\mathrm{A}]_{\mathrm{eq}} + (k'_{\mathrm{a}})^2$$

introduce $[A]_{tot} = [A]_{eq} + 2[A_2]_{eq}$ into the middle term,

$$\frac{1}{\tau^2} \approx 16k_a^2[A]_{eq}^2 + 8k_a k_a'([A]_{tot} - 2[A_2]_{eq}) + (k_a')^2$$

$$\approx 16k_a^2[A]_{eq}^2 + 8k_a k_a'[A]_{tot} - 16k_a k_a'[A_2]_{eq} + (k_a')^2 = \boxed{8k_a k_a'[A]_{tot} + (k_a')^2}$$

and use the equilibrium condition again to see that the remaining equilibrium concentrations cancel each other.

COMMENT. Introducing $[A]_{tot}$ into just one term of eqn (i) above is a permissible step but not a very systematic one. It is worth trying because of the resemblance between eqn (i) and the desired expression: we would be finished if we could get $[A]_{tot}$ into the middle term and somehow get the first term to disappear! A more systematic but messier approach would be to express $[A]_{eq}$ in terms of the desired $[A]_{tot}$ by using the equilibrium condition and $[A]_{tot} = [A]_{eq} + 2[A_2]_{eq}$. Solve both of those equations for $[A_2]_{eq}$, set the two resulting expressions equal to each other, solve for $[A]_{eq}$ in terms of the desired $[A]_{tot}$, and substitute *that* expression for $[A]_{eq}$ everywhere in eqn (i).

(b) Plot $\dfrac{1}{\tau^2}$ vs. $[A]_{tot}$

The resulting curve should be a straight line whose *y*-intercept is $(k_a')^2$ and whose slope is $8k_a k_a'$.

(c) Draw up the following table:

$[A]_{tot}/(\text{mol dm}^{-3})$	0.500	0.352	0.251	0.151	0.101
τ/ns	2.3	2.7	3.3	4.0	5.3
$1/(\tau/\text{ns})^2$	0.189	0.137	0.092	0.062	0.036

The plot is shown in Figure 21.4.

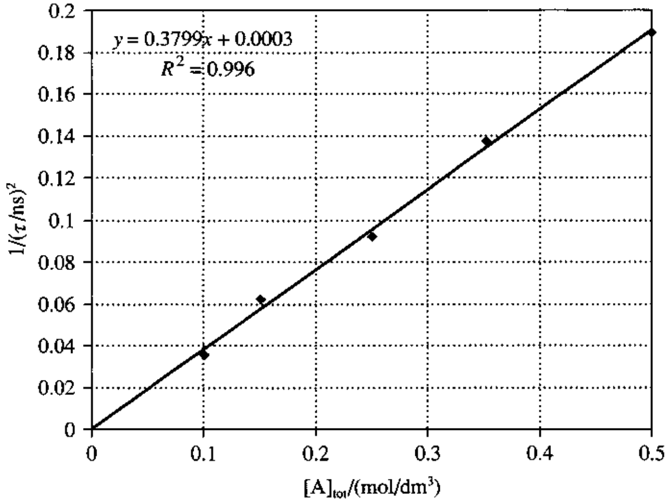


Figure 21.4

The y-intercept is 0.0003 $\mathrm{ns^{-2}}$ and the slope is 0.38 $\mathrm{ns^{-2}\,dm^3\,mol^{-1}}$, so

$$k_\mathrm{a}' = \{3\times10^{-4}\times(10^{-9}\,\mathrm{s})^{-2}\}^{1/2} = (3\times10^{14}\,\mathrm{s^{-2}})^{1/2} = \boxed{1.\bar{7}\times10^{7}\,\mathrm{s^{-1}}}$$

$$k_\mathrm{a} = \frac{0.38\times(10^{-9}\,\mathrm{s})^{-2}\,\mathrm{dm^3\,mol^{-1}}}{8\times(1.\bar{7}\times10^{7}\,\mathrm{s^{-1}})} = \boxed{2.\bar{7}\times10^{9}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

and $$K = \frac{k_\mathrm{a}/\mathrm{dm^3\,mol^{-1}\,s^{-1}}}{k_\mathrm{a}'/\mathrm{s^{-1}}} = \frac{2.\bar{7}\times10^{9}}{1.\bar{7}\times10^{7}} = \boxed{1.\bar{6}\times10^{2}}$$

COMMENT. The data define a good straight line, as the correlation coefficient $R^2 = 0.996$ shows. That straight line appears to go through the origin, but the best-fit equation gives a small non-zero y-intercept. Inspection of the plot shows that several of the data points lie about as far from the fit line as the y-intercept does from zero. This suggests that the y-intercept has a fairly high relative uncertainty and so do the rate constants.

P21.18 (a) The fluorescence intensity is proportional to the concentration of fluorescing species, so

$$\frac{I_\mathrm{f}}{I_0} = \frac{[\mathrm{S}]}{[\mathrm{S}]_0} = \mathrm{e}^{-t/\tau_0}\,[21.79] \quad \text{so} \quad \ln\left(\frac{I_\mathrm{f}}{I_0}\right) = -\frac{t}{\tau_0}$$

A plot of $\ln(I_\mathrm{f}/I_0)$ against t should be linear with a slope equal to $-1/\tau_0$ (i.e. $\tau_0 = -1/\text{slope}$) and an intercept equal to zero. See Figure 21.5. The plot is linear, with slope $-0.150\ \mathrm{ns^{-1}}$, so

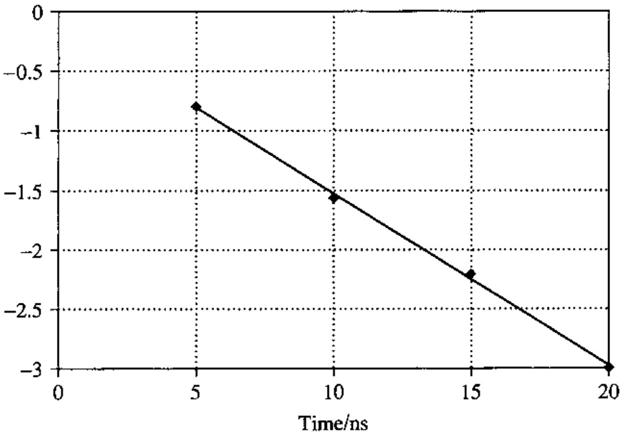


Figure 21.5

$$\tau_0 = -1/(-0.15\bar{0}\ \mathrm{ns^{-1}}) = \boxed{6.7\ \mathrm{ns}}$$

Alternatively, average the experimental values of $\frac{1}{t}\ln\left(\frac{I_\mathrm{f}}{I_0}\right)$ and check that the standard deviation is a small fraction of the average (it is). The average equals $-1/\tau_0$ (i.e. $\tau_0 = -1/\text{average}$).

(b) The quantum yield for fluorescence is related to the rate constants for the various decay mechanisms of the excited state by

$$\phi_\mathrm{f} = \frac{k_\mathrm{f}}{k_\mathrm{f} + k_\mathrm{ISC} + k_\mathrm{IC}}\,[21.81] = k_\mathrm{f}\tau_0\,[21.80]$$

so $k_\mathrm{f} = \phi_\mathrm{f}/\tau_0 = 0.70/(6.7\ \mathrm{ns}) = \boxed{0.10\bar{5}\ \mathrm{ns^{-1}}}$

P21.20 Proceed as in Problem 21.18. In the absence of a quencher, a plot of $\ln I_f/I_0$ against t should be linear with a slope equal to $-1/\tau_0$. The plot is in fact linear with a best-fit slope of $-0.100\bar{4}\ \mu\text{s}^{-1}$ (See Figure 21.6.)

$$\tau_0 = \frac{-1}{-0.100\bar{4}\ \mu\text{s}^{-1}} = 9.96\ \mu\text{s}$$

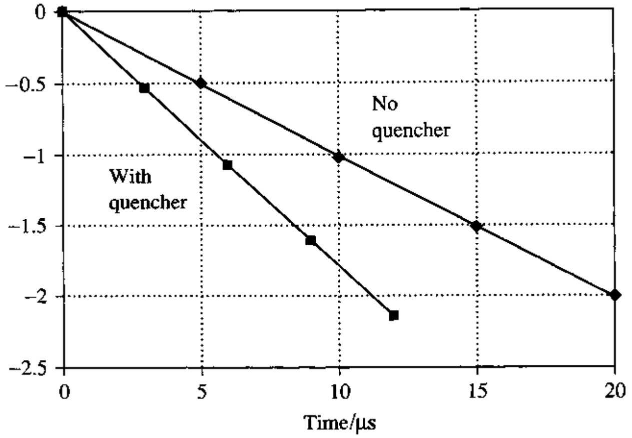


Figure 21.6

In the presence of a quencher, a graph of $\ln I_f/I_0$ against t is still linear but with a slope equal to $-1/\tau$. This plot is found to be linear with a regression slope equal to $-1.78\bar{8}\ \mu\text{s}^{-1}$.

$$\tau = \frac{-1}{-0.178\bar{8}\ \mu\text{s}^{-1}} = 5.59\ \mu\text{s}$$

The rate constant for quenching (i.e. for energy transfer to the quencher) can be obtained from

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_Q[\text{Q}]\ \text{[Example 21.9]}$$

Thus,
$$k_Q = \frac{\tau^{-1} - \tau_0^{-1}}{[\text{N}_2]} = \frac{RT(\tau^{-1} - \tau_0^{-1})}{p_{\text{N}_2}}$$
$$= \frac{(0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})(300\ \text{K})(0.1788 - 0.1004) \times (10^{-6}\ \text{s})^{-1}}{9.74 \times 10^{-4}\ \text{atm}}$$
$$= \boxed{1.98 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

Solutions to theoretical problems

P21.22 The rate of change of [A] is

$$\frac{\text{d[A]}}{\text{d}t} = -k_r[\text{A}]^n$$

Hence,
$$\int_{[\text{A}]_0}^{[\text{A}]} \frac{\text{d[A]}}{[\text{A}]^n} = -k_r \int_0^t \text{d}t = -k_r t$$

Therefore, $k_r t = \left(\dfrac{1}{n-1}\right) \times \left(\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right)$

At $t = t_{1/2}$, $[A] = [A]_0/2$

$$k_r t_{1/2} = \left(\frac{1}{n-1}\right) \times \left(\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) = \left(\frac{2^{n-1}-1}{n-1}\right) \times \left(\frac{1}{[A]_0^{n-1}}\right)$$

and $t_{1/2} = \boxed{\dfrac{2^{n-1}-1}{k_r(n-1)[A]_0^{n-1}}}$ [as in Table 21.3]

Now, let $t_{1/3}$ be the time at which $[A] = [A]_0/3$. Substitute these expressions into the integrated rate law:

$$k_r t_{1/3} = \left(\frac{1}{n-1}\right) \times \left(\frac{3^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) = \left(\frac{3^{n-1}-1}{n-1}\right) \times \left(\frac{1}{[A]_0^{n-1}}\right)$$

and $t_{1/3} = \boxed{\dfrac{3^{n-1}-1}{k_r(n-1)[A]_0^{n-1}}}$

P21.24 $v = \dfrac{d[P]}{dt} = k_r[A][B]$

Let the initial concentrations be $[A]_0 = A_0$, $[B]_0 = B_0$, and $[P]_0 = 0$. Then, when P is formed in concentration x, the concentration of A changes to $A_0 - 2x$ and that of B changes to $B_0 - 3x$. Therefore,

$$\frac{d[P]}{dt} = \frac{dx}{dt} = k_r(A_0 - 2x)(B_0 - 3x) \quad \text{with } x = 0 \text{ at } t = 0$$

$$\int_0^t k_r dt = \int_0^x \frac{dx}{(A_0 - 2x) \times (B_0 - 3x)}$$

Apply partial fractions decomposition to the integrand on the right:

$$\int_0^t k_r dt = \int_0^x \left(\frac{6}{2B_0 - 3A_0}\right) \times \left(\frac{1}{3(A_0 - 2x)} - \frac{1}{2(B_0 - 3x)}\right) dx$$

$$= \left(\frac{-1}{(2B_0 - 3A_0)}\right) \times \left(\int_0^x \frac{dx}{x - \frac{1}{2}A_0} - \int_0^x \frac{dx}{x - \frac{1}{3}B_0}\right)$$

$$k_r t = \left(\frac{-1}{(2B_0 - 3A_0)}\right) \times \left[\ln\left(\frac{x - \frac{1}{2}A_0}{-\frac{1}{2}A_0}\right) - \ln\left(\frac{x - \frac{1}{3}B_0}{-\frac{1}{3}B_0}\right)\right]$$

$$= \left(\frac{-1}{2B_0 - 3A_0}\right) \ln\left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)}\right) = \boxed{\left(\frac{1}{3A_0 - 2B_0}\right) \ln\left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)}\right)}$$

P21.26 Integrate eqn 21.30

$$E_a = -R\left(\frac{\mathrm{d}\ln k_r}{\mathrm{d}(1/T)}\right)$$

to find an expression for $\ln k_r$ as a function of temperature

$$\mathrm{d}\ln k_r = -\frac{E_a}{R}\mathrm{d}(1/T)$$

so $$\int \mathrm{d}\ln k_r = \int -\frac{E_a}{R}\mathrm{d}(1/T) = -\frac{E_a}{R}\int \mathrm{d}(1/T)$$

and $$\ln k_r = -\frac{E_a}{RT} + C$$

This is eqn 21.29, with $C = \ln A$.

P21.28 The rate law $\dfrac{\mathrm{d}[A]}{\mathrm{d}t} = -k_r[A]^n$ for $n \neq 1$ integrates to

$$k_r t = \left(\frac{1}{n-1}\right)\times\left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) \text{[Table 21.3]}$$

At $t = t_{1/2}$, $$kt_{1/2} = \left(\frac{1}{n-1}\right)\left[\left(\frac{2}{[A]_0}\right)^{n-1} - \left(\frac{1}{[A]_0}\right)^{n-1}\right]$$

At $t = t_{3/4}$, $$kt_{3/4} = \left(\frac{1}{n-1}\right)\left[\left(\frac{4}{3[A]_0}\right)^{n-1} - \left(\frac{1}{[A]_0}\right)^{n-1}\right]$$

Hence, $$\frac{t_{1/2}}{t_{3/4}} = \boxed{\frac{2^{n-1}-1}{(\frac{4}{3})^{n-1}-1}}$$

P21.30 $$2\,A \underset{k_r'}{\overset{k_r}{\rightleftharpoons}} A_2 \qquad \frac{\mathrm{d}[A]}{\mathrm{d}t} = -2k_r[A]^2 + 2k_r'[A_2]$$

Define the deviation from equilibrium, x, by the following equations, which satisfy the law of mass conservation:

$$[A] = [A]_{eq} + 2x \quad \text{and} \quad [A_2] = [A_2]_{eq} - x$$

Then,

$$\frac{\mathrm{d}([A]_{eq} + 2x)}{\mathrm{d}t} = -2k_r([A]_{eq} + 2x)^2 + 2k_r'([A_2]_{eq} - x)$$

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t} &= -k_r([A]_{eq} + 2x)^2 + k_r'([A_2]_{eq} - x) = -k_r([A]_{eq}^2 + 4[A]_{eq}x + 4x^2) + k_r'([A_2]_{eq} - x)\\ &= -\{4k_r x^2 + (k_r' + 4k_r[A]_{eq})x + k_r[A]_{eq}^2 - k_r'[A_2]_{eq}\}\\ &\approx -\{(k_r' + 4k_r[A]_{eq})x + k_r[A]_{eq}^2 - k_r'[A_2]_{eq}\}\end{aligned}$$

In the last equation the term containing x^2 has been dropped because x will be small near equilibrium and the x^2 term will be negligibly small. The equation may now be rearranged and integrated using the following integration, which is found in standard mathematical handbooks:

$$\int \frac{\mathrm{d}w}{aw+b} = \frac{1}{a}\ln(aw+b)$$

$$\int \frac{\mathrm{d}x}{(k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}})x + k_r[\mathrm{A}]_{\mathrm{eq}}^2 - k_r'[\mathrm{A}_2]_{\mathrm{eq}}} = -\int \mathrm{d}t$$

$$\frac{1}{(k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}})}\ln\{(k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}})x + k_r[\mathrm{A}]_{\mathrm{eq}}^2 - k_r'[\mathrm{A}_2]_{\mathrm{eq}}\} = -t + \text{constant}$$

Let $\ln\left(\frac{y}{y_0}\right) = -(k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}})t$, where $y = (k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}})x + k_r[\mathrm{A}]_{\mathrm{eq}}^2 - k_r'[\mathrm{A}_2]_{\mathrm{eq}}$

Then, $y = y_0\mathrm{e}^{-(k_r'+4k_r[\mathrm{A}]_{\mathrm{eq}})t}$

Comparison of the above exponential to the decay equation $y = y_0\mathrm{e}^{-t/\tau}$ reveals that

$$\tau = \boxed{\frac{1}{k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}}}}$$

COMMENT. Note that this equation can be used as the basis of an alternative derivation of the equation discussed in Problem 21.16. The manipulations use the facts that $K = [\mathrm{A}_2]_{\mathrm{eq}}/[\mathrm{A}]_{\mathrm{eq}}^2 = k_r/k_r'$ and $[\mathrm{A}]_{\mathrm{tot}} = [\mathrm{A}]_{\mathrm{eq}} + 2[\mathrm{A}_2]_{\mathrm{eq}}$ by conservation of mass, which can be used to show that

$$[\mathrm{A}]_{\mathrm{tot}} = [\mathrm{A}]_{\mathrm{eq}} + \frac{2k_r}{k_r'}[\mathrm{A}]_{\mathrm{eq}}^2 \quad \text{or} \quad \frac{2k_r}{k_r'}[\mathrm{A}]_{\mathrm{eq}}^2 + [\mathrm{A}]_{\mathrm{eq}} - [\mathrm{A}]_{\mathrm{tot}} = 0$$

This quadratic equation can be solved for $[\mathrm{A}]_{\mathrm{eq}}$:

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{k_r'}{4k_r}\left(\sqrt{1 + \frac{8k_r[\mathrm{A}]_{\mathrm{tot}}}{k_r'}} - 1\right)$$

Substitution of this equation into $\frac{1}{\tau^2} = (k_r' + 4k_r[\mathrm{A}]_{\mathrm{eq}})^2$ and some algebraic manipulation yields the result of Problem 21.16: $\frac{1}{\tau^2} = k_r'^2 + 8k_rk_r'[\mathrm{A}]_{\mathrm{tot}}$.

P21.32 (a) To find mean cube and mean square molar masses, we need an expression for the probability P_N that a polymer consists of N monomers. In stepwise polymerization, P_N is the probability that the polymer has $N-1$ reacted end groups and one unreacted end group. In terms of the fraction p of total end groups in the mixture that have reacted, the former probability is p^{N-1}; the latter $1-p$. Therefore, the total probability of finding an N-mer is

$$P_N = p^{N-1}(1-p)$$

Since the molar mass of an N-mer is N times the monomer mass, M_1, the mean square molar mass is

$$\begin{aligned}\langle M^2\rangle &= \sum_N (M_1N)^2P_N = M_1^2\sum_N N^2P_N = M_1^2\langle N^2\rangle = M_1^2(1-p)\sum_N N^2p^{N-1}\\ &= M_1^2(1-p)\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}\sum_N p^N = M_1^2(1-p)\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}(1-p)^{-1} = \frac{M_1^2(1+p)}{(1-p)^2}.\end{aligned}$$

Similarly, the mean cube molar mass is

$$\begin{aligned}\langle M^3\rangle &= \sum_N (M_1N)^3P_N = M_1^3(1-p)\sum_N N^3p^{N-1}\\ &= M_1^3(1-p)\frac{\mathrm{d}}{\mathrm{d}p}\sum_N N^2p^N = M_1^3(1-p)\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}\sum_N p^N\\ &= M_1^3(1-p)\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}(1-p)^{-1} = \frac{M_1^3(1+4p+p^2)}{(1-p)^3}\end{aligned}$$

Therefore, $\dfrac{\langle M^3\rangle}{\langle M^2\rangle} = \boxed{\dfrac{M_1(1+4p+p^2)}{1-p^2}}$

(b) $\langle N\rangle = \dfrac{1}{1-p}$ [21.68a], so $p = 1-\dfrac{1}{\langle N\rangle}$

$$\begin{aligned}\frac{\langle M^3\rangle}{\langle M^2\rangle} &= \frac{M_1\left\{1+4\left(1-\frac{1}{\langle N\rangle}\right)+\left(1-\frac{1}{\langle N\rangle}\right)^2\right\}}{1-\left(1-\frac{1}{\langle N\rangle}\right)^2}\\ &= \frac{M_1(\langle N\rangle^2+4\langle N\rangle^2-4\langle N\rangle+\langle N\rangle^2-2\langle N\rangle+1)}{\langle N\rangle^2-\langle N\rangle^2+2\langle N\rangle-1}\\ &= \boxed{\frac{M_1(6\langle N\rangle^2-6\langle N\rangle+1)}{2\langle N\rangle-1}}.\end{aligned}$$

P21.34 $\dfrac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_\mathrm{r}[\mathrm{A}]^2[\mathrm{OH}] = -k_\mathrm{r}[\mathrm{A}]^3$ because $[\mathrm{A}] = [\mathrm{OH}]$

$\dfrac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^3} = -k_\mathrm{r}\mathrm{d}t$ and $\displaystyle\int_{[\mathrm{A}]_0}^{[\mathrm{A}]}\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^3} = -k_\mathrm{r}\int_0^t \mathrm{d}t = -k_\mathrm{r}t$

Since $\displaystyle\int\frac{\mathrm{d}x}{x^3} = \frac{-1}{2x^2}$, the equation becomes

$\dfrac{1}{[\mathrm{A}]^2} - \dfrac{1}{[\mathrm{A}]_0^2} = 2k_\mathrm{r}t$ or $[\mathrm{A}] = [\mathrm{A}]_0(1+2k_\mathrm{r}t[\mathrm{A}]_0^2)^{-1/2}$

By eqn 21.68a the degree of polymerization, $\langle N\rangle$, is given by

$$\langle N\rangle = \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = \boxed{(1+2k_\mathrm{r}t[\mathrm{A}]_0^2)^{1/2}}$$

P21.36 Consider the following mechanism:

$Cl_2 + h\nu \rightarrow 2\,Cl$	I_a
$Cl + CHCl_3 \rightarrow CCl_3 + HCl$	k_2
$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$	k_3
$2\,CCl_3 + Cl_2 \rightarrow 2\,CCl_4$	k_4

(i) $$\frac{d[CCl_4]}{dt} = 2k_4[CCl_3]^2[Cl_2] + k_3[CCl_3][Cl_2]$$

(ii) $$\frac{d[CCl_3]}{dt} = k_2[Cl][CHCl_3] - k_3[CCl_3][Cl_2] - 2k_4[CCl_3]^2[Cl_2] = 0$$

(iii) $$\frac{d[Cl]}{dt} = 2I_a - k_2[Cl][CHCl_3] + k_3[CCl_3][Cl_2] = 0$$

(iv) $$\frac{d[Cl_2]}{dt} = -I_a - k_3[CCl_3][Cl_2] - k_4[CCl_3]^2[Cl_2]$$

Therefore, $I_a = k_4[CCl_3]^2[Cl_2]$ [add eqns (ii) and (iii)]

which implies that

$$[CCl_3] = \left(\frac{I_a}{k_4[Cl_2]}\right)^{1/2}$$

Then, with (i),

$$\frac{d[CCl_4]}{dt} = 2I_a + \frac{k_3 I_a^{1/2}[Cl_2]^{1/2}}{k_4^{1/2}}$$

When the pressure of chlorine is high, and the initiation rate is slow (in the sense that the lowest powers of I_a dominate), the second term dominates the first, giving

$$\frac{d[CCl_4]}{dt} = \frac{k_3 I_a^{1/2}}{k_4^{1/2}}[Cl_2]^{1/2} = \boxed{k_r I_a^{1/2}[Cl_2]^{1/2}}$$

with $k_r = \dfrac{k_3}{k_4^{1/2}}$. It seems necessary to suppose that Cl + Cl recombination (which needs a third body) is unimportant.

Solutions to applications

P21.38 (a) For the mechanism

$$hhhh\ldots \underset{k_a'}{\overset{k_a}{\rightleftarrows}} hchh\ldots$$

$$hchh\ldots \underset{k_b'}{\overset{k_b}{\rightleftarrows}} cccc\ldots$$

the rate equations are

$$\frac{\mathrm{d}[hhhh\ldots]}{\mathrm{d}t} = -k_{\mathrm{a}}[hhhh\ldots] + k_{\mathrm{a}}'[hchh\ldots]$$

$$\frac{\mathrm{d}[hchh\ldots]}{\mathrm{d}t} = k_{\mathrm{a}}[hhhh\ldots] - k_{\mathrm{a}}'[hchh\ldots] - k_{\mathrm{b}}[hchh\ldots] + k_{\mathrm{b}}'[cccc\ldots]$$

$$\frac{\mathrm{d}[cccc\ldots]}{\mathrm{d}t} = k_{\mathrm{b}}[hchh\ldots] - k_{\mathrm{b}}'[cccc\ldots]$$

(b) Apply the steady-state approximation to the intermediate:

$$\frac{\mathrm{d}[hchh\ldots]}{\mathrm{d}t} = k_{\mathrm{a}}[hhhh\ldots] - k_{\mathrm{a}}'[hchh\ldots] - k_{\mathrm{b}}[hchh\ldots] + k_{\mathrm{b}}'[cccc\ldots] = 0$$

so $[hchh\ldots] = \dfrac{k_{\mathrm{a}}[hhhh\ldots] + k_{\mathrm{b}}'[cccc\ldots]}{k_{\mathrm{a}}' + k_{\mathrm{b}}}$

Therefore, $\dfrac{\mathrm{d}[hhhh\ldots]}{\mathrm{d}t} = -k_{\mathrm{a}}[hhhh\ldots] + k_{\mathrm{a}}'\left(\dfrac{k_{\mathrm{a}}[hhhh\ldots] + k_{\mathrm{b}}'[cccc\ldots]}{k_{\mathrm{a}}' + k_{\mathrm{b}}}\right)$

$$= [hhhh\ldots]\left(\frac{k_{\mathrm{a}}k_{\mathrm{a}}' - k_{\mathrm{a}}(k_{\mathrm{a}}' + k_{\mathrm{b}})}{k_{\mathrm{a}}' + k_{\mathrm{b}}}\right) + k_{\mathrm{a}}'\left(\frac{k_{\mathrm{b}}'[cccc\ldots]}{k_{\mathrm{a}}' + k_{\mathrm{b}}}\right)$$

$$= -\frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}' + k_{\mathrm{b}}}[hhhh\ldots] + \frac{k_{\mathrm{a}}'k_{\mathrm{b}}'}{k_{\mathrm{a}}' + k_{\mathrm{b}}}[cccc\ldots]$$

This rate expression may be compared to that given in the text [Section 21.4] for the mechanism $\mathrm{A} \underset{k_{\mathrm{r}}'}{\overset{k_{\mathrm{r}}}{\rightleftharpoons}} \mathrm{B}$

Here, $hhhh\ldots \underset{k_{\mathrm{eff}}'}{\overset{k_{\mathrm{eff}}}{\rightleftharpoons}} cccc\ldots$ with $k_{\mathrm{eff}} = \dfrac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}' + k_{\mathrm{b}}}$ $\quad k_{\mathrm{eff}}' = \dfrac{k_{\mathrm{a}}'k_{\mathrm{b}}'}{k_{\mathrm{a}}' + k_{\mathrm{b}}}$

P21.40 We approach the lifetime via the efficiency of resonant energy transfer:

$$\eta_{\mathrm{T}} = 1 - \frac{\phi_{\mathrm{f}}}{\phi_{\mathrm{f,0}}}\,[21.85] = 1 - \frac{\tau}{\tau_0}$$

and $\eta_{\mathrm{T}} = \dfrac{R_0^6}{R_0^6 + R^6}$ [21.86]

Equating these two expressions for η_{T} and solving for R gives:

$$\frac{R_0^6}{R_0^6 + R^6} = 1 - \frac{\tau}{\tau_0} = \frac{\tau_0 - \tau}{\tau_0} \quad \text{so} \quad \frac{R_0^6 + R^6}{R_0^6} = \frac{\tau_0}{\tau_0 - \tau}$$

$$\left(\frac{R}{R_0}\right)^6 = \frac{\tau_0}{\tau_0 - \tau} - 1 = \frac{\tau_0 - \tau_0 + \tau}{\tau_0 - \tau} = \frac{\tau}{\tau_0 - \tau} \quad \text{or} \quad R = R_0\left(\frac{\tau}{\tau_0 - \tau}\right)^{1/6}$$

$\tau/\tau_0 = 10\ \mathrm{ps}/10^3\ \mathrm{ps} = 0.010$ and $R = 5.6\ \mathrm{nm}\left(\dfrac{0.010}{1 - 0.010}\right)^{1/6} = \boxed{2.6\ \mathrm{nm}}$

22 Reaction dynamics

Answers to discussion questions

D22.2 A reaction in solution can be regarded as the outcome of two stages: one is the encounter of two reactant species; this is followed by their reaction in the second stage, if they acquire their activation energy. If the rate-determining step is the latter, then the reaction is activation controlled. An activation-controlled reaction is activated to the extent that the rate-limiting step has a significant activation energy.

If the rate-determining step is the coming together of the reactants, then the reaction is said to be diffusion controlled. For a reaction of the form A + B → P that obeys the second-order rate law $v = k_r[\mathrm{A}][\mathrm{B}]$, in the diffusion-controlled regime,

$$k_r = k_d = 4\pi R^* D N_A \ [22.18]$$

where D is the sum of the diffusion coefficients of the two reactant species and R^* is the distance at which reaction occurs. A further approximation is that each molecule obeys the Stokes–Einstein relationship and Stokes' law, and then

$$k_d \approx \frac{8RT}{3\eta} \ [22.21]$$

where η is the viscosity of the medium. The result suggests that k_d is independent of the radii of the reactants. It also suggests that the rate constant depends only weakly on temperature, so the activation energy is small.

D22.4 Much work in chemical dynamics is based on classical dynamical theories, in which trajectories on potential energy surfaces are important quantities. (By the way, this statement characterizes approaches to dynamic phenomena outside chemical reactions, such as protein folding to cite one example.) As we have learned, classical mechanics is a limiting case of the more generally accurate quantum mechanics, and in quantum mechanics trajectories are not valid constructs. Classical approaches are often computationally more tractable and conceptually simpler than quantum, which is why their use persists; however, classically based approaches increasingly diverge from quantum results for systems of low mass or at low temperature. Under such conditions, so-called tunnelling (the non-zero probability of a system to be in a state from which classical mechanics forbids it) is a quantum-mechanical effect too important to ignore.

Perhaps the most common application of quantum approaches to dynamics is in the calculation of potential energy surfaces. Quantum-chemical techniques are often used to derive potential-energy surfaces on which classical trajectories are then investigated. Quantum-mechanical scattering theory (Section 22.8d) is brought to bear in some cases.

D22.6 See Section 22.8, particularly subsection (b). In general, for a collision to become a reaction, the collision must have enough energy for the system to reach the 'height' of the transition state, the saddle point on the potential energy surface between the reactant and product 'valleys'. The collision must also have a trajectory that crosses the saddle point without returning to the reactants. (Remember, if a system has enough energy to reach the transition state, it has enough energy to go back to reactants!)

The position of the transition state in the potential energy 'landscape' influences the characteristics of trajectories that lead to reaction. See Figures 22.24 and 22.25 in the main text. For example, if the transition state lies nearer the reactants, the trajectories most likely to lead to reaction have reactants high in translational energy; once past the transition state, these trajectories roll from side to side of the product valley, yielding vibrationally excited products. Conversely, if the transition state lies nearer the products, then reactants with high translational energy are very likely to 'bounce off' the surface back into the reactant valley. It takes side-to-side motion (i.e. vibrational motion) to get the system around the corner to the transition state; once there, products with high translational energy are formed.

D22.8 For electron transfer to occur at an electrode, several steps are necessary. A species in a bulk solution phase must lose its solvating species and make its way through the electrode/solution interface to the electrode. Once there, its hydration sphere must be adjusted by the electron transfer itself, and then the species must detach and reverse its steps as it were, passing back through the interface into the bulk solution phase. Because there are energy requirements associated with these steps, they are said to be activated. How the activation Gibbs function depends on applied potentials and on the resemblance of transition state to oxidized and reduced species is examined in *Further information* 22.2.

Solutions to exercises

E22.1(b) The collision frequency is

$$z = \sigma\bar{c}_{\mathrm{rel}}\mathcal{N}[20.11\mathrm{a}]$$

where $\bar{c}_{\mathrm{rel}} = \left(\dfrac{8kT}{\pi\mu}\right)^{1/2} = 4\left(\dfrac{kT}{\pi m}\right)^{1/2}\left[20.10 \text{ with } \mu = \dfrac{m}{2}\right]$, $\sigma = \pi d^2$ [Section 20.1b] $= 4\pi R^2$, and $\mathcal{N} = \dfrac{p}{kT}$

Therefore, $z = \sigma\bar{c}_{\mathrm{rel}}\mathcal{N} = (4\pi R^2) \times \left(\dfrac{p}{kT}\right) \times 4\left(\dfrac{kT}{\pi m}\right)^{1/2} = 16pR^2\left(\dfrac{\pi}{mkT}\right)^{1/2}$

$$= 16 \times (100 \times 10^3\ \mathrm{Pa}) \times (180 \times 10^{-12}\ \mathrm{m})^2$$

$$\times \left(\frac{\pi}{(28.01 \times 1.661 \times 10^{-27}\ \mathrm{kg}) \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (298\ \mathrm{K})}\right)^{1/2}$$

$$= \boxed{6.64 \times 10^9\ \mathrm{s^{-1}}}$$

The collision density for like molecules is

$$Z = \frac{z\mathcal{N}}{2}\,[22.7\text{a}] = \frac{z}{2}\left(\frac{p}{kT}\right) = \frac{6.64\times10^{9}\ \text{s}^{-1}}{2}\left(\frac{100\times10^{3}\ \text{Pa}}{1.381\times10^{-23}\ \text{J K}^{-1}\times298\ \text{K}}\right) = \boxed{8.07\times10^{34}\ \text{s}^{-1}\,\text{m}^{-3}}$$

For the percentage increase at constant volume, note that $\mathcal{N}$ is constant at constant volume, so the only constant-volume temperature dependence on z (and on Z) is in the speed factor:

$$z \propto T^{1/2} \quad \text{so} \quad \frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_V = \frac{1}{2T} \quad \text{and} \quad \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_V = \frac{1}{2T}$$

Therefore, $\dfrac{\delta z}{z} = \dfrac{\delta Z}{Z} \approx \dfrac{\delta T}{2T} = \dfrac{1}{2}\left(\dfrac{10\ \text{K}}{298\ \text{K}}\right) = 0.017$

so both z and Z increase by about $\boxed{1.7\%}$.

E22.2(b) The fraction of collisions having at least E_a along the line of flight may be inferred by dividing out of the collision-theory rate constant [eqn. 22.12] those factors that can be identified as belonging to the collision rate: $f = e^{-E_a/RT}$.

(a) (i) $\dfrac{E_a}{RT} = \dfrac{15\times10^{3}\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(300\ \text{K})} = 6.01, \quad \text{so} \quad f = e^{-6.01} = \boxed{0.0024}$

(ii) $\dfrac{E_a}{RT} = \dfrac{15\times10^{3}\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(800\ \text{K})} = 2.26, \quad \text{so} \quad f = e^{-2.26} = \boxed{0.10}$

(b) (i) $\dfrac{E_a}{RT} = \dfrac{150\times10^{3}\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(300\ \text{K})} = 60.1, \quad \text{so} \quad f = e^{-60.1} = \boxed{7.6\times10^{-27}}$

(ii) $\dfrac{E_a}{RT} = \dfrac{150\times10^{3}\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(800\ \text{K})} = 22.6, \quad \text{so} \quad f = e^{-22.6} = \boxed{1.6\times10^{-10}}$

E22.3(b) A straightforward approach would be to compute $f = e^{-E_a/RT}$ at the new temperature and compare it to that at the old temperature. An approximate approach would be to note that f changes from $f_0 = e^{-E_a/RT}$ to $\exp\left(\dfrac{-E_a}{RT(1+x)}\right)$, where x is the fractional increase in the temperature. If x is small, the exponent changes from $-E_a/RT$ to approximately $-E_a(1-x)/RT$ and f changes from f_0 to

$$f \approx e^{-E_a(1-x)/RT} = e^{-E_a/RT}(e^{-E_a/RT})^{-x} = f_0 f_0^{-x}$$

Thus, the new fraction is the old one times a factor of f_0^{-x}. The increase in f expressed as a percentage is

$$\frac{f-f_0}{f_0}\times100\% = \frac{f_0 f_0^{-x} - f_0}{f_0}\times100\% = (f_0^{-x}-1)\times100\%$$

(a) (i) $f_0^{-x} = (2.4\times10^{-3})^{-10/300} = 1.22$ and the percentage change is $\boxed{22\%}$.

(ii) $f_0^{-x} = (0.10)^{-10/800} = 1.03$ and the percentage change is $\boxed{3\%}$.

(b) (i) $f_0^{-x} = (7.6\times10^{-27})^{-10/300} = 7.4$ and the percentage change is $\boxed{640\%}$ ($\boxed{600\%}$ using the exact approach).

(ii) $f_0^{-x} = (1.6\times10^{-10})^{-10/800} = 1.33$ and the percentage change is $\boxed{33\%}$.

E22.4(b) $k_r = P\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A e^{-E_a/RT}$ [22.13]

We are not given a steric factor, so assume that $P = 1$.

$$k_r = 0.30 \times (10^{-9}\,\text{m})^2 \times \left(\frac{8(1.381\times10^{-23}\,\text{J K}^{-1})\times(450\,\text{K})}{\pi\times(3.930\times1.661\times10^{-27}\,\text{kg})}\right)^{1/2}$$

$$\times (6.022\times10^{23}\,\text{mol}^{-1})\times\exp\left(\frac{-200\times10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(450\,\text{K})}\right)$$

$$= \boxed{1.7\times10^{-15}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}} = \boxed{1.7\times10^{-12}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}.$$

E22.5(b) According to the RRK model,

$$P = \left(1-\frac{E^*}{E}\right)^{s-1} \quad [22.14\text{a}]$$

where E is the available energy, E^* is the energy needed to break a bond, and s is the number of modes of motion available to accept the energy.

$$P = \left(1-\frac{250\,\text{kJ mol}^{-1}}{300\,\text{kJ mol}^{-1}}\right)^{6-1} = \boxed{1.3\times10^{-4}}$$

E22.6(b) The rate constant for a diffusion-controlled bimolecular reaction is

$k_d = 4\pi R^* D N_A$ [22.18]

where $D = D_A + D_B = 2\times(4.2\times10^{-9}\,\text{m}^2\,\text{s}^{-1}) = 8.4\times10^{-9}\,\text{m}^2\,\text{s}^{-1}$

$$k_d = 4\pi\times(0.50\times10^{-9}\,\text{m})\times(8.4\times10^{-9}\,\text{m}^2\,\text{s}^{-1})\times(6.022\times10^{23}\,\text{mol}^{-1})$$

$$k_d = 3.2\times10^{7}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} = \boxed{3.2\times10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

E22.7(b) The rate constant for a diffusion-controlled bimolecular reaction is

$$k_d = \frac{8RT}{3\eta}\,[22.21] = \frac{8\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K})}{3\eta} = \frac{6.61\times10^3\,\text{J mol}^{-1}}{\eta}$$

(a) For decylbenzene, $\eta = 3.36\,\text{cP} = 3.36\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}$

$$k_d = \frac{6.61\times10^3\,\text{J mol}^{-1}}{3.36\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}} = 1.97\times10^{6}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

$$= \boxed{1.97\times10^{9}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

(b) In concentrated sulfuric acid, $\eta = 27\,\text{cP} = 27\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}$

$$k_d = \frac{6.61\times10^3\,\text{J mol}^{-1}}{27\times10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}} = 2.4\times10^{5}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

$$= \boxed{2.4\times10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

E22.8(b) The rate constant for a diffusion-controlled bimolecular reaction is

$$k_{\mathrm{d}}=\frac{8RT}{3\eta}=\frac{8\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{3\times(0.601\times10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})}$$

$$=1.10\times10^{7}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}=\boxed{1.10\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

Since this reaction is elementary bimolecular it is second order, hence

$$t_{1/2}=\frac{1}{2k_{\mathrm{d}}[\mathrm{A}]_0}\ \text{[Table 21.3, with } k_{\mathrm{r}}=2k_{\mathrm{d}} \text{ because two atoms are consumed]}$$

$$\text{so}\quad t_{1/2}=\frac{1}{2\times(1.10\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\times(1.8\times10^{-3}\ \mathrm{mol\ dm^{-3}})}=\boxed{2.53\times10^{-8}\ \mathrm{s}}$$

E22.9(b) The steric factor, P, is

$$P=\frac{\sigma^*}{\sigma}\ \text{[Section 22.1(c)]}$$

The mean collision cross-section is $\sigma=\pi d^2$ with $d=(d_{\mathrm{A}}+d_{\mathrm{B}})/2$.

Get the diameters from the collision cross-sections:

$$d_{\mathrm{A}}=(\sigma_{\mathrm{A}}/\pi)^{1/2}\quad\text{and}\quad d_{\mathrm{B}}=(\sigma_{\mathrm{B}}/\pi)^{1/2}$$

$$\text{so}\quad \sigma=\frac{\pi}{4}\left\{\left(\frac{\sigma_{\mathrm{A}}}{\pi}\right)^{1/2}+\left(\frac{\sigma_{\mathrm{B}}}{\pi}\right)^{1/2}\right\}^2=\frac{(\sigma_{\mathrm{A}}^{1/2}+\sigma_{\mathrm{B}}^{1/2})^2}{4}=\frac{\{(0.88\ \mathrm{nm^2})^{1/2}+(0.40\ \mathrm{nm^2})^{1/2}\}^2}{4}=\boxed{0.62\ \mathrm{nm^2}}.$$

$$\text{Therefore, } P=\frac{8.7\times10^{-22}\ \mathrm{m^2}}{0.62\times(10^{-9}\ \mathrm{m})^2}=\boxed{1.41\times10^{-3}}$$

E22.10(b) Since the reaction is diffusion controlled, the rate-limiting step is bimolecular and therefore second order, hence

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]$$

$$\text{where}\quad k_{\mathrm{d}}=4\pi R^*DN_{\mathrm{A}}\,[22.18]=4\pi N_{\mathrm{A}}R^*(D_{\mathrm{A}}+D_{\mathrm{B}})$$

$$=4\pi N_{\mathrm{A}}\times(R_{\mathrm{A}}+R_{\mathrm{B}})\times\frac{kT}{6\pi\eta}\left(\frac{1}{R_{\mathrm{A}}}+\frac{1}{R_{\mathrm{B}}}\right)[22.20]=\frac{2RT}{3\eta}(R_{\mathrm{A}}+R_{\mathrm{B}})\times\left(\frac{1}{R_{\mathrm{A}}}+\frac{1}{R_{\mathrm{B}}}\right),$$

$$k_{\mathrm{d}}=\frac{2\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(293\ \mathrm{K})}{3\times(1.27\times10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})}\times(442+885)\times\left(\frac{1}{442}+\frac{1}{885}\right)$$

$$=5.76\times10^{6}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}=5.76\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

Therefore, the initial rate is

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=(5.76\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\times(0.200\ \mathrm{mol\ dm^{-3}})\times(0.150\ \mathrm{mol\ dm^{-3}})$$

$$=\boxed{1.73\times10^{8}\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$$

COMMENT. If the approximation of eqn 22.21 is used, $k_d = 5.12\times10^{9}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$. In this case the approximation results in a difference of just over 10% compared to the expression used above.

E22.11(b) For reactions in solution the relationship between energy and enthalpy of activation is

$\Delta^{\ddagger}H = E_a - RT$ [*Brief Comment* in Section 22.5(a)]

$$k_r = B\,e^{\Delta^{\ddagger}S/R}e^{-\Delta^{\ddagger}H/RT},\quad B = \left(\frac{kT}{h}\right)\times\left(\frac{RT}{p^{\ominus}}\right)\ [22.43]$$

$$= B\,e^{\Delta^{\ddagger}S/R}e^{-E_a/RT}e = A\,e^{-E_a/RT}$$

Therefore, $A \approx e\,B\,e^{\Delta^{\ddagger}S/R}$, implying that $\Delta^{\ddagger}S = R\left(\ln\dfrac{A}{B} - 1\right)$

Therefore, since $E_a = 6134\ \mathrm{K}\times R$

$$\Delta^{\ddagger}H \approx E_a - RT = (6134\ \mathrm{K} - 298\ \mathrm{K})R$$

$$= (5836\ \mathrm{K})\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{+48.52\ \mathrm{kJ\,mol^{-1}}}$$

$$B = \frac{(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})\times(298\ \mathrm{K})}{6.626\times10^{-34}\ \mathrm{J\,s}}\times\frac{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{10^{5}\ \mathrm{Pa}}$$

$$= 1.54\times10^{11}\ \mathrm{m^3\,mol^{-1}\,s^{-1}} = 1.54\times10^{14}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$$

and hence $\Delta^{\ddagger}S = (8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\times\left\{\ln\left(\dfrac{8.72\times10^{12}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}}{1.54\times10^{14}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}}\right) - 1\right\}$

$$= \boxed{-32.2\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

COMMENT. In this connection, the enthalpy of activation is often referred to as the 'energy' of activation.

E22.12(b) The enthalpy of activation for a bimolecular solution reaction is [Exercise 22.11(b)]

$$\Delta^{\ddagger}H = E_a - RT = 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}\times(5373\ \mathrm{K} - 298\ \mathrm{K}) = \boxed{+42.2\ \mathrm{kJ\,mol^{-1}}}$$

The entropy of activation is [Exercise 22.11(b)]

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right)$$

with $B = \dfrac{kRT^2}{hp^{\ominus}} = 1.54\times10^{14}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [Exercise 22.11(b)]

Therefore, $\Delta^{\ddagger}S = 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}\times\left\{\ln\left(\dfrac{6.45\times10^{13}}{1.54\times10^{14}}\right) - 1\right\} = -15.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$

Hence, $\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = \{42.2 - (298)\times(-15.5\times10^{-3})\}\ \mathrm{kJ\,mol^{-1}} = \boxed{+46.8\ \mathrm{kJ\,mol^{-1}}}$.

E22.13(b) Use eqn 22.44 to relate a bimolecular gas-phase rate constant to activation energy and entropy:

$$k_r = e^{2}B\,e^{\Delta^{\ddagger}S/R}e^{-E_a/RT}$$

where $$B=\left(\frac{kT}{h}\right)\times\left(\frac{RT}{p^{\ominus}}\right)[22.43]=\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(328\,\mathrm{K})^2\times(8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(10^5\,\mathrm{Pa})}$$

$$=1.86\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

Solve for the entropy of activation:

$$\Delta^{\ddagger}S=R\left(\ln\frac{k_\mathrm{r}}{B}-2\right)+\frac{E_\mathrm{a}}{T}$$

$$=8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times\left(\ln\frac{0.23\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}{1.86\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}-2\right)+\frac{49.6\times10^3\,\mathrm{J\,mol^{-1}}}{328\,\mathrm{K}}$$

$$=\boxed{-93\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E22.14(b) For a bimolecular gas-phase reaction,

$$\Delta^{\ddagger}S=R\left(\ln\frac{k_\mathrm{r}}{B}-2\right)+\frac{E_\mathrm{a}}{T}\ [\text{Exercise 22.13(b)}]$$

$$=R\left(\ln\frac{A}{B}-\frac{E_\mathrm{a}}{RT}-2\right)+\frac{E_\mathrm{a}}{T}=R\left(\ln\frac{A}{B}-2\right)$$

where $$B=\frac{kRT^2}{hp^{\ominus}}\ [\text{Exercise 22.11(a)}]$$

For two structureless particles, the rate constant is

$$k_\mathrm{r}=N_\mathrm{A}\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2}\mathrm{e}^{-\Delta_\mathrm{r}E_0/RT}\ [22.39]$$

The activation energy is [21.30]

$$E_\mathrm{a}=RT^2\frac{\mathrm{d}\ln k_\mathrm{r}}{\mathrm{d}T}=RT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\ln N_\mathrm{A}\sigma^*+\frac{1}{2}\ln\frac{8k}{\pi\mu}+\frac{1}{2}\ln T-\frac{\Delta_\mathrm{r}E_0}{RT}\right)$$

$$=RT^2\left(\frac{1}{2T}+\frac{\Delta_\mathrm{r}E_0}{RT^2}\right)=\Delta_\mathrm{r}E_0+\frac{RT}{2},$$

so the prefactor is

$$A=k_\mathrm{r}\mathrm{e}^{E_\mathrm{a}/RT}=N_\mathrm{A}\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2}\mathrm{e}^{-\Delta_\mathrm{r}E_0/RT}(\mathrm{e}^{\Delta_\mathrm{r}E_0/RT}\mathrm{e}^{1/2})=N_\mathrm{A}\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2}\mathrm{e}^{1/2}$$

Hence

$$\Delta^{\ddagger}S=R\left\{\ln N_\mathrm{A}\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2}+\frac{1}{2}-\ln\frac{kRT^2}{p^{\ominus}h}-2\right\}$$

$$=R\left\{\ln\frac{\sigma^*p^{\ominus}h}{(kT)^{3/2}}\left(\frac{8}{\pi\mu}\right)^{1/2}-\frac{3}{2}\right\}$$

For identical particles,

$$\mu = m/2 = (78 \times 1.661 \times 10^{-27}\ \text{kg})/2 = 6.5 \times 10^{-26}\ \text{kg}$$

and hence

$$\Delta^{\ddagger}S = 8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}$$
$$\times \left\{ \ln \frac{0.62 \times (10^{-9}\ \text{m})^2 \times 10^5\ \text{Pa} \times 6.626 \times 10^{-34}\ \text{J s}}{(1.381 \times 10^{-23}\ \text{J K}^{-1} \times 500\ \text{K})^{3/2}} \left(\frac{8}{\pi \times 6.5 \times 10^{-26}\ \text{kg}} \right)^{1/2} - \frac{3}{2} \right\}$$
$$= \boxed{-77\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

E22.15(b) At low pressure, the reaction can be assumed to be bimolecular. (See Section 21.8(a).)

(a) $\Delta^{\ddagger}S = R\left(\ln \dfrac{A}{B} - 2\right)$ [Exercise 22.14(b)]

where $B = \dfrac{kRT^2}{hp^{\ominus}} = \dfrac{1.381 \times 10^{-23}\ \text{J K}^{-1} \times 8.3145\ \text{J K}^{-1}\,\text{mol}^{-1} \times (298\ \text{K})^2}{6.626 \times 10^{-34}\ \text{J s} \times 10^5\ \text{Pa}}$

$= 1.54 \times 10^{11}\ \text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} = 1.54 \times 10^{14}\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$.

Hence, $\Delta^{\ddagger}S = 8.3145\ \text{J K}^{-1}\,\text{mol}^{-1} \times \left(\ln \dfrac{2.3 \times 10^{13}\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}{1.54 \times 10^{14}\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}} - 2 \right) = \boxed{-32\ \text{J K}^{-1}\,\text{mol}^{-1}}$

(b) The enthalpy of activation for a bimolecular gas-phase reaction is

$\Delta^{\ddagger}H = E_a - 2RT$ [*Brief Comment* in Section 22.5(a)]

$\Delta^{\ddagger}H = 30.0\ \text{kJ mol}^{-1} - 2 \times 8.3145\ \text{J mol}^{-1}\,\text{K}^{-1} \times 298\ \text{K} = \boxed{+25.0\ \text{kJ mol}^{-1}}$

(c) The Gibbs energy of activation at 298 K is

$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 25.0\ \text{kJ mol}^{-1} - (298\ \text{K}) \times (-32 \times 10^{-3}\ \text{kJ K}^{-1}\,\text{mol}^{-1})$

$\Delta^{\ddagger}G = \boxed{+34.7\ \text{kJ mol}^{-1}}$

E22.16(b) Use eqn 22.49 to examine the effect of ionic strength on a rate constant:

$\log k_r = \log k_r^{\circ} + 2Az_Az_BI^{1/2}$

Hence, $\log k_r^{\circ} = \log k_r - 2Az_Az_BI^{1/2} = \log 1.55 - 2 \times 0.509 \times (1 \times 1) \times (0.0241)^{1/2} = 0.032$

and $k_r^{\circ} = \boxed{1.08\ \text{dm}^6\,\text{mol}^{-2}\,\text{min}^{-1}}$.

E22.17(b) To solve this exercise requires some information left out of this edition of the textbook. See *Quanta, Matter, and Change* by Peter Atkins, Julio de Paula, and Ron Friedman (New York: WH Freeman, 2008). For a donor–acceptor pair separated by a constant distance, assuming that the reorganization energy is constant, eqn 20.62 in *Quanta, Matter, and Change* holds.

$$\ln k_{\text{et}} = -\frac{(\Delta_r G^{\ominus})^2}{4\lambda RT} - \frac{\Delta_r G^{\ominus}}{2RT} + \text{constant}$$

or, using molecular units rather than molar units,

$$\ln k_{\mathrm{et}} = -\frac{(\Delta_{\mathrm{r}}G^{\ominus})^2}{4\lambda kT} - \frac{\Delta_{\mathrm{r}}G^{\ominus}}{2kT} + \text{constant}$$

Two sets of rate constants and reaction Gibbs energies can be used to generate two equations (the above equation applied to the two sets) in two unknowns, λ and the constant.

$$\ln k_{\mathrm{et},1} + \frac{(\Delta_{\mathrm{r}}G_1^{\ominus})^2}{4\lambda kT} + \frac{\Delta_{\mathrm{r}}G_1^{\ominus}}{2kT} = \text{constant} = \ln k_{\mathrm{et},2} + \frac{(\Delta_{\mathrm{r}}G_2^{\ominus})^2}{4\lambda kT} + \frac{\Delta_{\mathrm{r}}G_2^{\ominus}}{2kT}$$

so $$\frac{(\Delta_{\mathrm{r}}G_1^{\ominus})^2 - (\Delta_{\mathrm{r}}G_2^{\ominus})^2}{4\lambda kT} = \ln\frac{k_{\mathrm{et},2}}{k_{\mathrm{et},1}} + \frac{\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus}}{2kT}$$

and $$\lambda = \frac{(\Delta_{\mathrm{r}}G_1^{\ominus})^2 - (\Delta_{\mathrm{r}}G_2^{\ominus})^2}{4kT\ln\frac{k_{\mathrm{et},2}}{k_{\mathrm{et},1}} + 2(\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus})}$$

$$\lambda = \frac{(-0.665\ \mathrm{eV})^2 - (-0.975\ \mathrm{eV})^2}{\frac{4(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}{1.602\times10^{-19}\ \mathrm{J\ eV^{-1}}}\ln\frac{3.33\times10^{6}}{2.02\times10^{5}} - 2(0.975-0.665)\ \mathrm{eV}} = \boxed{1.53\ \mathrm{eV}}$$

If we knew the activation Gibbs energy, we could use eqns 20.58 and 20.60 of *Quanta, Matter, and Change* to compute $H_{\mathrm{DA}}(r)$ from either rate constant, and we *can* compute the activation Gibbs energy from eqn. 22.61 (Atkins, Peter, and de Paula, Julio, *Physical Chemistry* (9th edn, Oxford: Oxford University Press, 2009)):

$$\Delta^{\ddagger}G = \frac{(\Delta_{\mathrm{r}}G^{\ominus} + \lambda)^2}{4\lambda} = \frac{\{(-0.665+1.53)\ \mathrm{eV}\}^2}{4(1.53\ \mathrm{eV})} = 0.123\ \mathrm{eV}$$

Now $$k_{\mathrm{et}} = \frac{2\{H_{\mathrm{DA}}(r)\}^2}{h}\left(\frac{\pi^3}{4\lambda kT}\right)^{1/2}\exp\left(\frac{-\Delta^{\ddagger}G}{kT}\right)$$

so $$H_{\mathrm{DA}}(r) = \left(\frac{hk_{\mathrm{et}}}{2}\right)^{1/2}\left(\frac{4\lambda kT}{\pi^3}\right)^{1/4}\exp\left(\frac{\Delta^{\ddagger}G}{2kT}\right)$$

$$= \left(\frac{(6.626\times10^{-34}\ \mathrm{J\ s})(2.02\times10^{5}\ \mathrm{s^{-1}})}{2}\right)^{1/2}$$

$$\times\left(\frac{4(1.53\ \mathrm{eV})(1.602\times10^{-19}\ \mathrm{J\ eV^{-1}})(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}{\pi^3}\right)^{1/4}$$

$$\times\exp\left(\frac{(0.123\ \mathrm{eV})(1.602\times10^{-19}\ \mathrm{J\ eV^{-1}})}{2(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}\right)$$

$$= \boxed{9.6\times10^{-24}\ \mathrm{J}}.$$

E22.18(b) For the same donor and acceptor at different distances, eqn 22.63 applies:

$$\ln k_{\mathrm{et}} = -\beta r + \text{constant}$$

The slope of a plot of $\ln k_{\mathrm{et}}$ versus r is $-\beta$. The slope of a line defined by two points is:

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\ln k_{\mathrm{et},2} - \ln k_{\mathrm{et},1}}{r_2 - r_1} = -\beta = \frac{\ln 4.51\times 10^5 - \ln 2.02\times 10^5}{(1.23-1.11)\ \mathrm{nm}}$$

so $\beta = -6.7\ \mathrm{nm}^{-1}$

Rearrange eqn 22.63 to solve for the constant and substitute one of the known values of k_{et}:

$$\begin{aligned}\text{constant} &= \ln k_{\mathrm{et}}/\mathrm{s}^{-1} + \beta r = \ln 2.02\times 10^5 + (-6.7\ \mathrm{nm}^{-1})\times(1.11\ \mathrm{nm})\\ &= 4.8\end{aligned}$$

Thus, when $r = 1.48$ nm,

$$\ln k_{\mathrm{et}}/\mathrm{s}^{-1} = -(6.7\ \mathrm{nm}^{-1})\times(1.48\ \mathrm{nm}) + 4.8 = 14.7$$

and $k_{\mathrm{et}} = \mathrm{e}^{14.7}\ \mathrm{s}^{-1} = \boxed{2.4\times 10^6\ \mathrm{s}^{-1}}$.

E22.19(b) The conditions are in the limit of large, positive overpotentials, so eqn 22.70 applies:

$$\ln j = \ln j_0 + (1-\alpha)f\eta$$

where $f = \dfrac{F}{RT} = \dfrac{96845\ \mathrm{C\ mol}^{-1}}{(8.3145\ \mathrm{J\ K}^{-1}\,\mathrm{mol}^{-1})\times(298\ \mathrm{K})} = 38.9\ \mathrm{V}^{-1}$

Subtracting this equation from the same relationship between another set of currents and overpotentials, we have

$$\ln\frac{j'}{j} = (1-\alpha)f(\eta' - \eta)$$

which rearranges to

$$\eta' = \eta + \frac{\ln(j'/j)}{(1-\alpha)f} = (105\times 10^{-3}\ \mathrm{V}) + \frac{\ln(72/17.0)}{(1-0.42)\times(38.9\ \mathrm{V})^{-1}} = \boxed{0.169\ \mathrm{V}}$$

E22.20(b) Take antilogarithms of eqn 22.70, then

$$j_0 = j\,\mathrm{e}^{-(1-\alpha)\eta f} = (17.0\ \mathrm{mA\ cm}^{-2})\times \mathrm{e}^{-(1-0.42)\times 0.105\ \mathrm{V}\times 38.9/\mathrm{V}} = \boxed{1.59\ \mathrm{mA\ cm}^{-2}}$$

E22.21(b) In the high overpotential limit

$$j = j_0\mathrm{e}^{(1-\alpha)f\eta}\ [22.69] \quad \text{so} \quad \frac{j_1}{j_2} = \mathrm{e}^{(1-\alpha)f(\eta_1-\eta_2)} \quad \text{and} \quad j_2 = j_1\mathrm{e}^{(1-\alpha)f(\eta_2-\eta_1)}$$

So, the current density at 0.60 V is

$$j_2 = (1.22\ \mathrm{mA\ cm}^{-2})\times \mathrm{e}^{(1-0.50)\times(0.60\ \mathrm{V}-0.50\ \mathrm{V})\times(38.9/\mathrm{V})} = \boxed{8.5\ \mathrm{mA\ cm}^{-2}}$$

E22.22(b) (a) The Butler–Volmer equation [22.65] is

$$\begin{aligned}j &= j_0(\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta})\\ &= (2.5\times 10^{-3}\ \mathrm{A\ cm}^{-2})\times(\mathrm{e}^{(1-0.58)\times(0.30\ \mathrm{V})\times(38.9/\mathrm{V})} - \mathrm{e}^{-0.58\times(0.30\mathrm{V})\times(38.9/\mathrm{V})}) = \boxed{0.34\ \mathrm{A\ cm}^{-2}}\end{aligned}$$

(b) Eqn 22.69 (also known as the Tafel equation) corresponds to the neglect of the second exponential above, which is very small for an overpotential of 0.3 V. (Even when it was kept, in part (a), it was negligible.) Hence,

$$j = \boxed{0.34\ \mathrm{A\ cm^{-2}}}$$

The validity of the Tafel equation increases with higher overpotentials, but decreases at lower overpotentials. A plot of j against η becomes linear (non-exponential) as $\eta \to 0$.

The validity of the Tafel equation improves as the overpotential increases.

E22.23(b) The Butler–Volmer equation [22.65], with transfer coefficients from Table 22.3, is

$$j = j_0(\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta}) = j_0(\mathrm{e}^{0.42f\eta} - \mathrm{e}^{-0.58f\eta})$$

Recall that η is the overpotential, defined as the working potential E' minus the zero-current potential E. The latter is given by the Nernst equation (6.27):

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q = E^{\ominus} - \frac{1}{f}\ln\frac{a(\mathrm{Fe^{2+}})}{a(\mathrm{Fe^{3+}})} = 0.77\ \mathrm{V} - \frac{1}{f}\ln\frac{a(\mathrm{Fe^{2+}})}{a(\mathrm{Fe^{3+}})}$$

Thus, $\eta = E' - 0.77\ \mathrm{V} + \dfrac{1}{f}\ln\dfrac{a(\mathrm{Fe^{2+}})}{a(\mathrm{Fe^{3+}})} = E' - 0.77\ \mathrm{V} + \dfrac{1}{f}\ln r,$

where r is the ratio of activities. Specializing to the condition that the ions have equal activities yields

$$\eta = E' - 0.77\ \mathrm{V}$$

and $j = (2.5\ \mathrm{mA\ cm^{-2}}) \times (\mathrm{e}^{0.42fE' - 0.42f\times 0.77\mathrm{V}} - \mathrm{e}^{-0.58fE' + 0.58f\times 0.77\mathrm{V}})$

Evaluating the constant parts of the exponentials (with $f = 38.9\ \mathrm{V^{-1}}$) and incorporating them as numerical factors yields

$$j = \boxed{(8.6\times 10^{-6}\,\mathrm{mA\ cm^{-2}}) \times \mathrm{e}^{0.42fE'} - (8.8\times 10^{-7}\ \mathrm{mA\ cm^{-2}})\mathrm{e}^{-0.58fE'}}$$

E22.24(b) The current density of electrons is j_0/e because each one carries a charge of magnitude e. Look up j_0 values in Table 22.3, and recall that $1\ \mathrm{A} = 1\ \mathrm{C\ s^{-1}}$.

For $\mathrm{Cu}\,|\,\mathrm{H_2}\,|\,\mathrm{H^+}$ $j_0 = 1.0\times 10^{-6}\ \mathrm{A\ cm^{-2}}$

$$\frac{j_0}{e} = \frac{1.0\times 10^{-6}\ \mathrm{A\ cm^{-2}}}{1.602\times 10^{-19}\ \mathrm{C}} = \boxed{6.2\times 10^{12}\ \mathrm{cm^{-2}\ s^{-1}}}$$

For $\mathrm{Pt}\,|\,\mathrm{Ce^{4+}},\mathrm{Ce^{3+}}$ $j_0 = 4.0\times 10^{-5}\ \mathrm{mA\ cm^{-2}}$

$$\frac{j_0}{e} = \frac{4.0\times 10^{-5}\ \mathrm{A\ cm^{-2}}}{1.602\times 10^{-19}\ \mathrm{C}} = \boxed{2.5\times 10^{14}\ \mathrm{cm^{-2}\ s^{-1}}}$$

There are approximately $\dfrac{(1.0\times 10^{-2}\ \mathrm{m})^2}{(260\times 10^{-12}\ \mathrm{m})^2} = 1.5\times 10^{15}$ atoms in each square centimetre of surface.

The numbers of electrons per atom are therefore $\boxed{4.2\times 10^{-3}\ \mathrm{s^{-1}}}$ and $\boxed{0.17\ \mathrm{s^{-1}}}$, respectively.

E22.25(b) When the overpotential is small, its relationship to the current density is

$$\eta = \frac{RTj}{Fj_0}\,[22.68] = \frac{j}{fj_0},$$

which implies that the current through surface area S is

$$I = Sj = Sj_0 f\eta$$

An ohmic resistance r obeys $\eta = Ir$, and so we can identify the resistance as

$$r = \frac{\eta}{I} = \frac{1}{Sj_0 f} = \frac{1}{1.0\ \text{cm}^2 \times 38.9\ \text{V}^{-1} \times j_0}$$

$$= \frac{2.57 \times 10^{-2}\ \Omega}{(j_0/\text{A cm}^{-2})}\,[1\ \text{V} = 1\ \text{A}\ \Omega]$$

(a) $\text{Pb}\,|\,\text{H}_2\,|\,\text{H}^+ \quad j_0 = 5.0 \times 10^{-12}\ \text{A cm}^{-2}$

$$r = \frac{2.57 \times 10^{-2}\ \Omega}{5.0 \times 10^{-12}} = \boxed{5.1 \times 10^{9}\ \Omega} = 5.1\ \text{G}\Omega$$

(b) $\text{Pt}\,|\,\text{Fe}^{3+}, \text{Fe}^{2+} \quad j_0 = 2.5 \times 10^{-3}\ \text{mA cm}^{-2}$

$$r = \frac{2.57 \times 10^{-2}\ \Omega}{2.5 \times 10^{-3}} = \boxed{10\ \Omega}$$

E22.26(b) Zn can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2}. The exchange current, according to the high negative overpotential limit, is

$$j = -j_0 \text{e}^{-\alpha f \eta}\,[22.71] = -(0.79\ \text{mA cm}^{-2}) \times \text{e}^{-0.5\times(38.9/\text{V})\times(-0.76\ \text{V})} = -2.1 \times 10^{6}\ \text{mA cm}^{-2}$$

This current density is much too large to allow deposition of zinc; that is, H_2 would begin being evolved, and quickly, long before zinc began to deposit.

Solutions to problems

Solutions to numerical problems

P22.2 Draw up the following table as the basis of an Arrhenius plot [21.29]:

T/K	600	700	800	1000
10^3 K/T	1.67	1.43	1.25	1.00
$k_r/(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	4.6×10^2	9.7×10^3	1.3×10^5	3.1×10^6
$\ln(k_r/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	6.13	9.18	11.8	14.9

The points are plotted in Figure 22.1.

The least-squares intercept is at 28.3, which implies that

$$A/(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = \text{e}^{28.3} = 2.0 \times 10^{12}$$

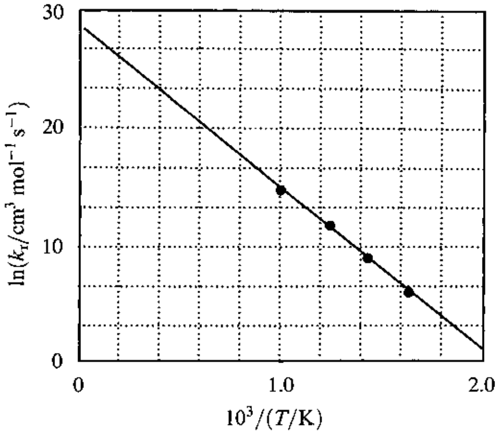


Figure 22.1

But comparison of eqn 22.13 to the Arrhenius equation tells us that $A = N_A P\sigma\left(\dfrac{8kT}{\pi\mu}\right)^{1/2}$, so

$$P = \frac{A}{N_A\sigma}\left(\frac{\pi\mu}{8kT}\right)^{1/2}$$

The reduced mass is

$$\mu = m(\mathrm{NO_2})/2 = (46 \times 1.661 \times 10^{-27}\,\mathrm{kg})/2 = 3.8 \times 10^{-26}\,\mathrm{kg}$$

so, evaluating P in the centre of the range of temperatures spanned by the data,

$$P = \frac{2.0 \times 10^{12} \times (10^{-2}\,\mathrm{m})^3\,\mathrm{mol^{-1}\,s^{-1}}}{(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times 0.60 \times (10^{-9}\,\mathrm{m})^2} \times \left(\frac{\pi \times 3.8 \times 10^{-26}\,\mathrm{kg}}{8 \times 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 800\,\mathrm{K}}\right)^{1/2}$$

$$= \boxed{6.5 \times 10^{-3}}.$$

$$\sigma^* = P\sigma = (6.5 \times 10^{-3}) \times (0.60\,\mathrm{nm^2}) = \boxed{3.9 \times 10^{-3}\,\mathrm{nm^2}} = 3.9 \times 10^{-21}\,\mathrm{m^2}$$

P22.4 Draw up the following table for an Arrhenius plot [21.29]:

$\theta/°\mathrm{C}$	−24.82	−20.73	−17.02	−13.00	−8.95
T/K	248.33	252.42	256.13	260.15	264.20
$10^3\,\mathrm{K}/T$	4.027	3.962	3.904	3.844	3.785
$10^4\,k_r/\mathrm{s^{-1}}$	1.22	2.31	4.39	8.50	14.3
$\ln(k_r/\mathrm{s^{-1}})$	−9.01	−8.37	−7.73	−7.07	−6.55

The points are plotted in Figure 22.2.

A least-squares fit of the data yields the intercept +32.7 at $1/T = 0$, which implies that $\ln\left(\dfrac{A}{\mathrm{s^{-1}}}\right) = 32.7$, and hence that $A = 1.53 \times 10^{14}\,\mathrm{s^{-1}}$. The slope is $-1.035 \times 10^4\,\mathrm{K} = -E_a/R$, and hence $\boxed{E_a = 86.0\,\mathrm{kJ\,mol^{-1}}}$.

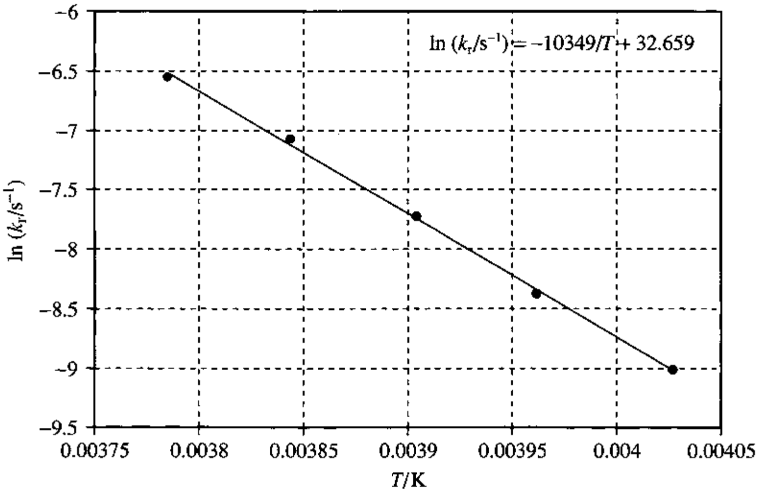


Figure 22.2

In solution $\Delta^\ddagger H = E_a - RT$ [*Brief comment* in Section 22.5(a)], so at −20°C

$$\Delta^\ddagger H = 86.0\ \text{kJ mol}^{-1} - (8.3145\ \text{J mol}^{-1}\,\text{K}^{-1}) \times (253\ \text{K})$$

$$= \boxed{+83.9\ \text{kJ mol}^{-1}}$$

We assume that the reaction is first order for which, by analogy to Section 22.4

$$K^\ddagger = \frac{kT}{h\nu^\ddagger}\bar{K}^\ddagger \quad \text{and} \quad k_r = k^\ddagger K^\ddagger = \nu^\ddagger \times \frac{kT}{h\nu^\ddagger} \times \bar{K}^\ddagger$$

with $\Delta^\ddagger G = -RT \ln \bar{K}^\ddagger$ [22.40]

Therefore, $k_r = A\mathrm{e}^{-E_a/RT} = \dfrac{kT}{h}\mathrm{e}^{-\Delta^\ddagger G/RT} = \dfrac{kT}{h}\mathrm{e}^{\Delta^\ddagger S/R}\mathrm{e}^{-\Delta^\ddagger H/RT}$

We can identify $\Delta^\ddagger S$ by writing

$$k_r = \frac{kT}{h}\mathrm{e}^{\Delta^\ddagger S/R}\,\mathrm{e}^{-E_a/RT}\,\mathrm{e} = A\mathrm{e}^{-E_a/RT}$$

and hence obtain

$$\Delta^\ddagger S = R\left\{\ln\left(\frac{hA}{kT}\right) - 1\right\}$$

$$= 8.3145\ \text{J K}^{-1}\,\text{mol}^{-1} \times \left\{\ln\left(\frac{(6.626 \times 10^{-34}\ \text{J s}) \times (1.53 \times 10^{14}\ \text{s}^{-1})}{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (253\ \text{K})}\right) - 1\right\}$$

$$= \boxed{+19.6\ \text{J K}^{-1}\,\text{mol}^{-1}}.$$

Therefore, $\Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S = 83.9\ \text{kJ mol}^{-1} - 253\ \text{K} \times 19.6\ \text{J K}^{-1}\,\text{mol}^{-1} = \boxed{+79.0\ \text{kJ mol}^{-1}}$.

P22.6 Figure 22.3 shows that $\log k_r$ is proportional to the ionic strength even when one of the reactants is a neutral molecule.

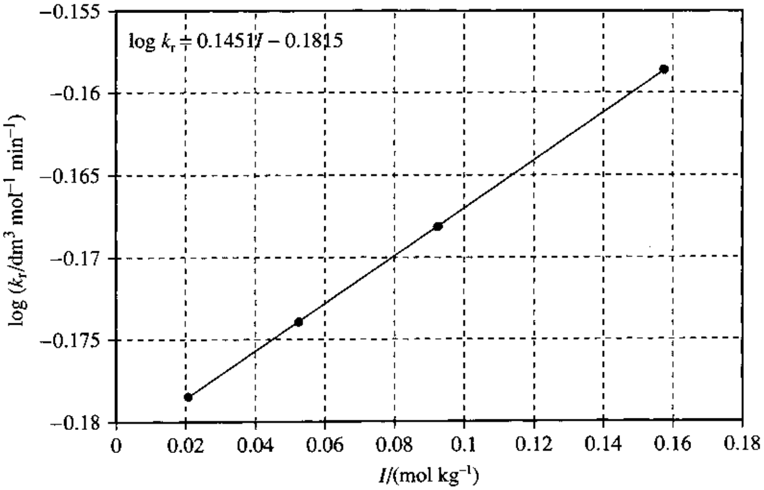


Figure 22.3

From the graph, the intercept at $I = 0$ is −0.182, so the limiting value of k_r is

$$k_r^\circ = 10^{-0.182} = \boxed{0.658\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}}$$

Compare the equation of the best-fit line to the logarithm of eqn 22.47b:

$$\log k_r = \log k_r^\circ - \log K_\gamma = \log k_r^\circ - \log\frac{\gamma_{C^\ddagger}}{\gamma_{I^-}\gamma_{H_2O_2}} = \log k_r^\circ + \log\frac{\gamma_{I^-}\gamma_{H_2O_2}}{\gamma_{C^\ddagger}}$$

which implies that $\log\frac{\gamma_{I^-}\gamma_{H_2O_2}}{\gamma_{C^\ddagger}} = 0.145I$.

If the Debye–Hückel limiting law holds (an approximation at best), the activity coefficients of I^- and the activated complex are equal, which would imply that $\log\gamma_{H_2O_2} = 0.145I$.

P22.8 Linear regression analysis of ln(rate constant) against $1/T$ yields the following results:

$$\ln(k_r/22.4\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}) = C + B/T$$

where $C = 34.36$ (standard deviation 0.36),

$B = -23227$ K (standard deviation 252 K),

and $R = 0.99976$ (indicating a good fit).

$$\ln(k_r'/22.4\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}) = C' + B'/T$$

where $C' = 28.30$ (standard deviation = 0.84),

$B' = -21065$ K (standard deviation = 582 K),

and $R = 0.99848$ (indicating a good fit).

The regression parameters can be used in the calculation of the pre-exponential factor (A) and the activation energy (E_a) using $\ln k_r = \ln A - E_a/RT$.

$$\ln A = C + \ln(22.4) = 37.47$$

so $A = 1.87 \times 10^{16}\,\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1} = \boxed{3.12 \times 10^{14}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$

$$E_a = -RB = -(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (-23227\ \text{K}) \times \left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right) = \boxed{193\ \text{kJ mol}^{-1}}$$

$$\ln A' = C' + \ln(22.4) = 31.41$$

so $A' = 4.37 \times 10^{13}\,\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1} = \boxed{7.29 \times 10^{11}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$

$$E_a' = -RB' = -(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (-21065\ \text{K}) \times \left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right) = \boxed{175\ \text{kJ mol}^{-1}}$$

To summarize:

	$A/(\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
Forward reaction	3.12×10^{14}	193
Reverse reaction	7.29×10^{11}	175

Both sets of data, k_r and k_r', fit the Arrhenius equation very well and are thus consistent with the collision theory of bimolecular gas-phase reactions that provides an equation [22.13] compatible with the Arrhenius equation. The numerical values for A' and A may be compared to the results of Example 22.1. The pre-exponential factor for the reverse reaction is comparable to the one estimated in that problem based on collision density; however, the prefactor for the forward reaction appears to be much larger than collision density. These data are not really compatible with collision theory.

P22.10 Deposition may occur when the potential falls to below E. (Recall that $\eta < 0$ for cathodic processes.) E is given by the Nernst equation [6.27]:

$$E = E^\ominus + \frac{RT}{zF}\ln a(\text{M}^+)$$

Simultaneous deposition will occur if the two potentials are the same; hence the relative activities are given by

$$E^\ominus(\text{Sn}, \text{Sn}^{2+}) + \frac{RT}{2F}\ln a(\text{Sn}^{2+}) = E^\ominus(\text{Pb}, \text{Pb}^{2+}) + \frac{RT}{2F}\ln a(\text{Pb}^{2+})$$

or $\ln\dfrac{a(\text{Sn}^{2+})}{a(\text{Pb}^{2+})} = \left(\dfrac{2F}{RT}\right)\{E^\ominus(\text{Pb}, \text{Pb}^{2+}) - E^\ominus(\text{Sn}, \text{Sn}^{2+})\} = 2 \times (38.9\ \text{V}^{-1}) \times (-0.126 + 0.136)\text{V} = 0.78$

That is, we require $a(\text{Sn}^{2+}) = \text{e}^{0.78}a(\text{Pb}^{2+}) = 2.2a(\text{Pb}^{2+})$.

P22.12 The thickness of the double layer is

$$r_D = \left(\frac{\varepsilon RT}{2\rho F^2 I b^\ominus}\right)^{1/2} \quad [18.16]$$

where $I = \dfrac{1}{2}\sum_i z_i^2(b_i/b^\circ)$, $b^\circ = 1\ \mathrm{mol\ kg^{-1}}$

For NaCl, $Ib^\circ = b_{\mathrm{NaCl}} \approx [\mathrm{NaCl}]$ assuming complete dissociation.

For Na_2SO_4, $Ib^\circ = \frac{1}{2}((1)^2(2b_{\mathrm{Na_2SO_4}}) + (2)^2 b_{\mathrm{Na_2SO_4}}) = 3b_{\mathrm{Na_2SO_4}} \approx 3[\mathrm{Na_2SO_4}]$,

also assuming complete dissociation.

We need the relative permittivity of water

$$\varepsilon = \varepsilon_r\varepsilon_0 = 78.54 \times (8.854 \times 10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}) = 6.954 \times 10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}$$

$$r_D \approx \left(\frac{(6.954 \times 10^{-10}\ \mathrm{J^{-1}\,C^2\,m^{-1}}) \times (8.3145\ \mathrm{J\ K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}{2 \times (1000\ \mathrm{kg\ m^{-3}}) \times (96485\ \mathrm{C\ mol^{-1}})^2}\right)^{1/2} \times \left(\frac{1}{Ib^\circ}\right)^{1/2}$$

$$\approx \frac{3.04 \times 10^{-10}\ \mathrm{m\ mol^{1/2}\,kg^{-1/2}}}{(Ib^\circ)^{1/2}} \approx \frac{304\ \mathrm{pm\ mol^{1/2}\,kg^{-1/2}}}{(Ib^\circ)^{1/2}}$$

These equations can be used to produce the graph of r_D against b_{salt} shown in Figure 22.4. Note the contraction of the double layer with increasing ionic strength.

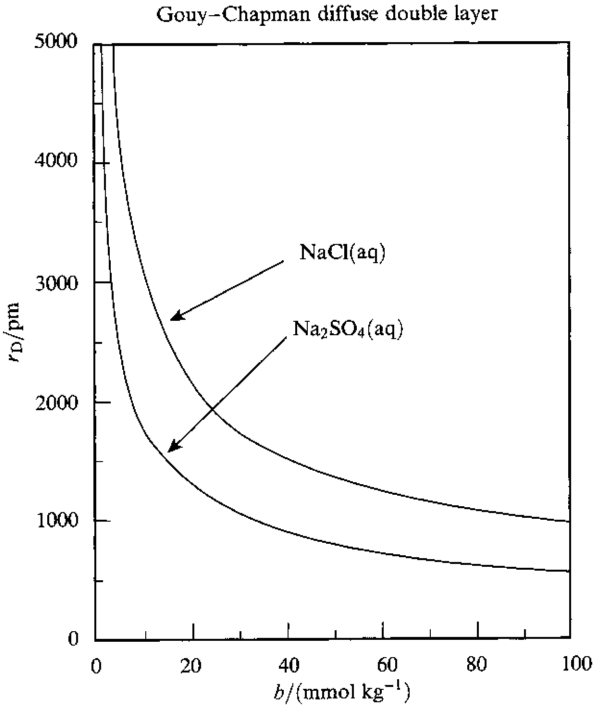


Figure 22.4

P22.14 At large positive values of the overpotential the current density is anodic.

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta})\ [22.65] \approx j_0 e^{(1-\alpha)f\eta}\ [22.69] = j_a\ [22.93]$$

$$\ln j = \ln j_0 + (1-\alpha)f\eta \quad \text{anode}$$

Performing a linear regression analysis of $\ln j$ against η, we find

$$\text{slope} = (1-\alpha)f = 19.550\ \text{V}^{-1}, \quad \text{standard deviation} = 0.355$$

$$y\text{-intercept} = \ln\{j_0/(\text{mA m}^{-2})\} = -10.826, \quad \text{standard deviation} = 0.287$$

$$R = 0.99901$$

$$j_0 = \text{e}^{-10.826}\ \text{mA m}^{-2} = \boxed{2.00\times10^{-5}\ \text{mA m}^{-2}}$$

$$\alpha = 1 - \frac{19.550\ \text{V}^{-1}}{f} = 1 - \frac{19.550\ \text{V}^{-1}}{38.9\ \text{V}^{-1}} = \boxed{0.498}$$

The linear regression explains 99.90% of the variation in a $\ln j$ against η plot and standard deviations are low. There are essentially $\boxed{\text{no}}$ deviations from the Tafel equation/plot.

Solutions to theoretical problems

P22.16 We are to show that

$$[\text{J}]^* = k_\text{r}\int_0^t [\text{J}]\text{e}^{-k_\text{r}t}\,\text{d}t + [\text{J}]\text{e}^{-k_\text{r}t}$$

is a solution of eqn 22.25,

$$\frac{\partial[\text{J}]^*}{\partial t} = D\frac{\partial^2[\text{J}]^*}{\partial x^2} - k_\text{r}[\text{J}]^*$$

(subject to the stated initial condition and boundary condition) provided that [J] is a solution of

$$\frac{\partial[\text{J}]}{\partial t} = D\frac{\partial^2[\text{J}]}{\partial x^2}$$

First, evaluate the derivatives of [J]*:

$$\frac{\partial[\text{J}]^*}{\partial t} = k_\text{r}[\text{J}]\text{e}^{-k_\text{r}t} + \left(\frac{\partial[\text{J}]}{\partial t}\right)\text{e}^{-k_\text{r}t} - k_\text{r}[\text{J}]\text{e}^{-k_\text{r}t} = \left(\frac{\partial[\text{J}]}{\partial t}\right)\text{e}^{-k_\text{r}t}$$

$$\text{and}\quad \frac{\partial^2[\text{J}]^*}{\partial x^2} = k_\text{r}\int_0^t\left(\frac{\partial^2[\text{J}]}{\partial x^2}\right)\text{e}^{-k_\text{r}t}\,\text{d}t + \left(\frac{\partial^2[\text{J}]}{\partial x^2}\right)\text{e}^{-k_\text{r}t}$$

$$\text{Thus,}\quad D\frac{\partial^2[\text{J}]^*}{\partial x^2} = k_\text{r}\int_0^t\left(\frac{\partial[\text{J}]}{\partial t}\right)\text{e}^{-k_\text{r}t}\,\text{d}t + \left(\frac{\partial[\text{J}]}{\partial t}\right)\text{e}^{-k_\text{r}t} = k_\text{r}\int_0^t\left(\frac{\partial[\text{J}]^*}{\partial t}\right)\text{d}t + \frac{\partial[\text{J}]^*}{\partial t}$$

The integral on the right is

$$\int_0^t\left(\frac{\partial[\text{J}]^*}{\partial t}\right)\text{d}t = [\text{J}]^* - [\text{J}]^*_0 = [\text{J}]^*$$

where we have used the initial condition that requires [J] and therefore also [J]* to be zero initially.

Thus, $D\dfrac{\partial^2[\mathrm{J}]^*}{\partial x^2} = k_\mathrm{r}[\mathrm{J}]^* + \dfrac{\partial[\mathrm{J}]^*}{\partial t}$

which is equivalent to eqn 22.25.

P22.18 The equilibrium constant, assuming unit activity coefficient for the neutral HA, is

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]\gamma_\mathrm{HA}}\gamma_\pm^2 \approx \frac{[\mathrm{H}^+][\mathrm{A}^-]\gamma_\pm^2}{[\mathrm{HA}]}$$

Therefore, $[\mathrm{H}^+] = \dfrac{[\mathrm{HA}]K_\mathrm{a}}{[\mathrm{A}^-]\gamma_\pm^2}$

and $\log[\mathrm{H}^+] = \log K_\mathrm{a} + \log\dfrac{[\mathrm{HA}]}{[\mathrm{A}^-]} - 2\log\gamma_\pm = \boxed{\log K_\mathrm{a} + \log\dfrac{[\mathrm{HA}]}{[\mathrm{A}^-]} + 2AI^{1/2}}$

Write $v = k_\mathrm{r}[\mathrm{H}^+][\mathrm{B}]$.

Then, $\log v = \log(k_\mathrm{r}[\mathrm{B}]) + \log[\mathrm{H}^+]$

$$= \log(k_\mathrm{r}[\mathrm{B}]) + \log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} + 2AI^{1/2} + \log K_\mathrm{a}$$

Call the rate in the limit of zero ionic strength v° (i.e. involving the terms other than I), then

$$\log v = \log v^\circ + 2AI^{1/2}$$

That is, the logarithm of the rate should depend linearly on the square root of the ionic strength.

$$\log\frac{v}{v^\circ} = 2AI^{1/2} \quad \text{so} \quad v = \boxed{v^\circ \times 10^{2AI^{1/2}}}$$

That is, the rate depends exponentially on the square root of the ionic strength.

P22.20 $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}^\ddagger \rightarrow \mathrm{P}$

$$k_\mathrm{r} = \left(\kappa\frac{kT}{h}\right) \times \bar{K}_\mathrm{c}^\ddagger[22.37\mathrm{b}] = \left(\kappa\frac{kT}{h}\right) \times \left(\frac{N_\mathrm{A}RT}{p^\ominus}\right)\frac{\bar{q}_{\mathrm{C}^\ddagger}^\ominus}{q_\mathrm{A}^\ominus q_\mathrm{B}^\ominus}\mathrm{e}^{-\Delta E_0/RT}[22.36]$$

We assume that the only factor that changes between the atomic and molecular case is the ratio of the partition functions.

For collisions between atoms

$$q_\mathrm{A}^\ominus = q_\mathrm{A}^\mathrm{T} \approx 10^{26} \approx q_\mathrm{B}^\ominus = q_\mathrm{B}^\mathrm{T}$$

$$\bar{q}_{\mathrm{C}^\ddagger}^\ominus = (q_\mathrm{C}^\mathrm{R})^2 q_\mathrm{C}^\mathrm{T} \approx (10^{1.5})^2 \times (10^{26}) = 10^{29}$$

$$k_\mathrm{r}(\text{atoms}) \propto \frac{10^{29}}{10^{26} \times 10^{26}} = 10^{-23}$$

For collisions between non-linear molecules

$$q_\mathrm{A}^\ominus = (q_\mathrm{A}^\mathrm{R})^3(q_\mathrm{A}^\mathrm{V})^{3N-6}(q_\mathrm{A}^\mathrm{T}) \approx (10^{1.5})^3 \times (1) \times (10^{26}) = 3 \times 10^{30} \approx q_\mathrm{B}^\ominus$$

$$\bar{q}^{\ominus}_{C\ddagger} = (q^{R}_{C})^{3}(q^{V}_{C})^{3(N+N')-7}(q^{T}_{C}) \approx (10^{1.5})^{3} \times (1) \times (10^{26}) = 3 \times 10^{30}$$

$$k_r(\text{molecules}) \propto \frac{3 \times 10^{30}}{1 \times 10^{61}} = 3 \times 10^{-31}$$

Therefore, $\dfrac{k_r(\text{atoms})}{k_r(\text{molecules})} \approx \dfrac{10^{-23}}{3 \times 10^{-31}} = \boxed{3 \times 10^{7}}$

P22.22 Start from the Butler–Volmer equation [22.65] and expand it in powers of η:

$$\begin{aligned} j &= j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}) \\ &= j_0\{1 + (1-\alpha)\eta f + \tfrac{1}{2}(1-\alpha)^2\eta^2 f^2 + \cdots -1 + \alpha f\eta - \tfrac{1}{2}\alpha^2\eta^2 f^2 + \cdots\} \\ &= j_0\{\eta f + \tfrac{1}{2}(\eta f)^2(1-2\alpha) + \cdots\} \end{aligned}$$

Average over one cycle (of period $2\pi/\omega$):

$$\langle j\rangle = j_0\{\langle\eta\rangle f + \tfrac{1}{2}(1-2\alpha)f^2\langle\eta^2\rangle + \cdots\}$$

where $\langle\eta\rangle = 0$, because $\dfrac{\omega}{2\pi}\displaystyle\int_0^{2\pi/\omega} \cos\omega t\,\mathrm{d}t = 0$

$\langle\eta^2\rangle = \tfrac{1}{2}\eta_0^2$, because $\dfrac{\omega}{2\pi}\displaystyle\int_0^{2\pi/\omega} \cos^2\omega t\,\mathrm{d}t = \tfrac{1}{2}$

Therefore, $\langle j\rangle = \boxed{\tfrac{1}{4}(1-2\alpha)f^2 j_0\eta_0^2}$

and $\langle j\rangle = 0$ when $\alpha = \tfrac{1}{2}$. For the mean current,

$$\begin{aligned} \langle I\rangle &= \tfrac{1}{4}(1-2\alpha)f^2 S j_0\eta_0^2 \\ &= \frac{1-0.76}{4} \times (1.0\ \text{cm}^2) \times (7.90 \times 10^{-4}\ \text{A cm}^{-2}) \times (0.0389\ \text{mV}^{-1}) \times (10\ \text{mV})^2 \\ &= \boxed{7.2\ \mu A} \end{aligned}$$

Solutions to applications

P22.24 Collision theory gives for a rate constant with no energy barrier

$$k_r = P\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A\ [22.13] \quad \text{so} \quad P = \frac{k_r}{\sigma N_A}\left(\frac{\pi\mu}{8kT}\right)^{1/2}$$

$$\begin{aligned} P &= \frac{k_r/(\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) \times (10^{-3}\,\text{m}^3\,\text{dm}^{-3})}{(\sigma/\text{nm}^2) \times (10^{-9}\,\text{m})^2 \times (6.022 \times 10^{23}\,\text{mol}^{-1})} \\ &\quad \times \left(\frac{\pi \times (\mu/m_u) \times (1.66 \times 10^{-27}\,\text{kg})}{8 \times (1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}\right)^{1/2} \\ &= \frac{(6.61 \times 10^{-13})k_r/(\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1})}{(\sigma/\text{nm}^2) \times (\mu/m_u)^{1/2}} \end{aligned}$$

The collision cross-section is

$$\sigma_{AB} = \pi d_{AB}^2, \quad \text{where } d_{AB} = \frac{1}{2}(d_A + d_B) = \frac{\sigma_A^{1/2} + \sigma_B^{1/2}}{2\pi^{1/2}} \quad \text{so} \quad \sigma_{AB} = \frac{(\sigma_A^{1/2} + \sigma_B^{1/2})^2}{4}$$

The collision cross-section for O_2 is listed in the Table 20.1. We would not be far wrong if we took that of the ethyl radical to equal that of ethene; similarly, we will take that of cyclohexyl to equal that of benzene. For O_2 with ethyl

$$\sigma = \frac{(0.40^{1/2} + 0.64^{1/2})^2}{4}\,\text{nm}^2 = 0.51\,\text{nm}^2$$

$$\mu = \frac{m_O m_{et}}{m_O + m_{et}} = \frac{(32.0m_u) \times (29.1m_u)}{(32.0 + 29.1)m_u} = 15.2m_u$$

$$\text{so} \quad P = \frac{(6.61 \times 10^{-13}) \times (4.7 \times 10^9)}{(0.51) \times (15.2)^{1/2}} = \boxed{1.6 \times 10^{-3}}$$

For O_2 with cyclohexyl

$$\sigma = \frac{(0.40^{1/2} + 0.88^{1/2})^2}{4}\,\text{nm}^2 = 0.62\,\text{nm}^2$$

$$\mu = \frac{m_O m_C}{m_O + m_C} = \frac{(32.0m_u) \times (77.1m_u)}{(32.0 + 77.1)m_u} = 22.6m_u$$

$$\text{so} \quad P = \frac{(6.61 \times 10^{-13}) \times (8.4 \times 10^9)}{(0.62) \times (22.6)^{1/2}} = \boxed{1.8 \times 10^{-3}}$$

P22.26 Eqn 22.49 may be written in the form

$$z_A^2 = \frac{1}{2A}\frac{\log(k_r/k_r^\circ)}{I^{1/2}}$$

where we have used $z_A = z_B$ for the cationic protein. This equation suggests that z_A can be determined through analysis that uses the mean value of $\frac{\log(k_r/k_r^\circ)}{I^{1/2}}$ from several experiments over a range of various ionic strengths:

$$z_A = \sqrt{\frac{1}{2A}\left\langle\frac{\log(k_r/k_r^\circ)}{I^{1/2}}\right\rangle}$$

We draw up a table that contains the data rows needed for the computation [$b^\circ = 1$ mol kg^{-1}]:

I/b°	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
k_r/k_r°	8.10	13.30	20.50	27.80	38.10	52.00
$\log(k_r/k_r^\circ)/(I/b^\circ)^{0.5}$	9.08	9.18	9.28	9.13	9.13	9.17

$$\left\langle \frac{\log(k_r/k_r^\circ)}{I^{1/2}} \right\rangle = 9.16$$

$$z_A = \sqrt{\frac{1}{2A}\left\langle \frac{\log(k_r/k_r^\circ)}{I^{1/2}} \right\rangle} = \sqrt{\frac{9.16}{2(0.509)}} = \boxed{+3.0}$$

We used the positive root because the protein is cationic.

P22.28 The theoretical treatment of Section 22.9 applies only at relatively high temperatures. At temperatures above 130 K, the reaction in question is observed to follow a temperature dependence consistent with eqn 22.62, namely increasing rate with increasing temperature. Below 130 K, the temperature-dependent terms in eqn 22.62 are replaced by temperature-independent wavefunction overlap integrals. The reaction proceeds primarily through tunnelling involving *nuclear* wavefunctions. See the end of Section 22.9(b).

23 Catalysis

Answers to discussion questions

D23.2 (a) Enzyme-catalyzed reactions that require minutes or hours may be followed with standard spectroscopic methods, including UV-visible, infrared, fluorescence, and NMR techniques. It may even be possible to determine the progression of substrate consumption, or product formation, with a chemical titration or radioactivity assay. Electrical conductivity may be used when ions are reaction participants; pH measurements are used to follow the reaction rate when an acid or base is a participant. An inhibitor that binds very strongly to the active site may be used to quench the reaction at any time, thereby making it possible to separate substrate and product with a chromatographic method; after which spectroscopic techniques, and the application of the Beer–Lambert law, may prove useful in the case for which substrate and product have overlapping spectra.

A stopped-flow technique provides for the rapid mixing that is necessary to follow reactions that require milliseconds or minutes. Standard spectroscopic, conductivity, or pH measurements are used to follow the reaction rate.

Very fast reactions may be followed by disturbing an equilibrium system with the excitation energy of flash photolysis or by a very sudden temperature jump initiated with a large current burst through the reaction solution. A pulsed laser beam is subsequently used to generate absorption, emission, or fluorescence spectra and the evolution of such spectra yields reaction rates.

(b) The initial rate of an enzyme-catalyzed reaction is acquired by extrapolation of the time evolution of observed rates to the initial mixing time. When repeated over a range of initial substrate concentrations, it is possible to prepare a double reciprocal, **Lineweaver–Burk plot** of $1/v_0$ against $1/[S]_0$. It is the intercept and slope of this plot that provides the values of the maximum reaction rate and the Michaelis constant (see eqn 23.3b). The manner in which an enzyme inhibitor alters the slope and intercept provides both evidence for the type of inhibition (competitive, uncompetitive, or non-competitive) and values of inhibitor binding constants (see eqn 23.8).

(c) The molecular shape of a strongly enzyme-binding, competitive inhibitor gives clues about the intermediate enzyme–substrate activated complex because, like the inhibitor, the activated ES complex must bind strongly to the active site in order to initiate reaction. Clues include charge distribution, hydrogen bonding, and hydrophobic interactions. The idea of a transition-state intermediate involves a slight modification of the Michaelis–Menten mechanism:

$$\mathrm{E + S \rightleftharpoons ES \rightleftharpoons ES^* \rightarrow EP \rightleftharpoons E + P}$$

The activated transition-state enzyme–substrate complex, ES*, is a very short lived intermediate because it has the activation energy necessary to react. It has been shown that the enzyme has a higher affinity for the transition-state intermediate than for the substrate and will bind the intermediate more strongly. Good inhibitors are generally transition-state analogues.

D23.4 Text Figure 23.6 summarizes the important characteristics of the three major modes of enzyme inhibition: competitive inhibition, uncompetitive inhibition, and non-competitive inhibition. Mathematical models for inhibition, which are the analogues of the Michaelis–Menten and Lineweaver–Burk equations [23.3a and 23.3b], are presented in eqns 23.7 and 23.8.

$$\frac{1}{v}=\frac{\alpha'}{v_{\max}}+\left(\frac{\alpha K_{\mathrm{M}}}{v_{\max}}\right)\frac{1}{[\mathrm{S}]_0}\ [23.8], \quad \text{where} \quad \alpha=1+[\mathrm{I}]/K_{\mathrm{I}} \quad \text{and} \quad \alpha'=1+[\mathrm{I}]/K_{\mathrm{I}}'$$

$$K_{\mathrm{I}}=[\mathrm{E}][\mathrm{I}]/[\mathrm{EI}],\ K_{\mathrm{I}}'=[\mathrm{ES}][\mathrm{I}]/[\mathrm{ESI}]$$

In **competitive inhibition** the inhibitor binds only to the active site of the enzyme and thereby inhibits the attachment of the substrate. This condition corresponds to $\alpha > 1$ and $\alpha' = 1$ (because ESI does not form). The slope of the Lineweaver–Burk plot increases by a factor of α relative to the slope for data on the uninhibited enzyme ($\alpha = \alpha' = 1$). The y-intercept does not change as a result of competitive inhibition.

In **uncompetitive inhibition** the inhibitor binds to a site of the enzyme that is removed from the active site, but only if the substrate is already present. The inhibition occurs because ESI reduces the concentration of ES, the active type of the complex. In this case $\alpha = 1$ (because EI does not form) and $\alpha' > 1$. The y-intercept of the Lineweaver–Burk plot increases by a factor of α' relative to the y-intercept for data on the uninhibited enzyme, but the slope does not change.

In **non-competitive inhibition** (also called **mixed inhibition**) the inhibitor binds to a site other than the active site, and its presence reduces the ability of the substrate to bind to the active site. Inhibition occurs at both the E and ES sites. This condition corresponds to $\alpha > 1$ and $\alpha' > 1$. Both the slope and y-intercept of the Lineweaver–Burk plot increase on addition of the inhibitor. Figure 23.6c shows the special case of $K_{\mathrm{I}} = K_{\mathrm{I}}'$ and $\alpha = \alpha'$, which results in intersection of the lines at the x-axis.

In all cases, the efficiency of the inhibitor may be obtained by determining K_{M} and $v_{\max}$ from a control experiment with uninhibited enzyme and then repeating the experiment with a known concentration of inhibitor. From the slope and y-intercept of the Lineweaver–Burk plot for the inhibited enzyme [eqn 23.8], the mode of inhibition, the values of α or α', and the values of K_{I}, or K_{I}' may be obtained.

D23.6 The characteristic conditions of the **Langmuir isotherm** are:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform.
3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites.

For the **BET isotherm** condition number 1 above is removed and the isotherm applies to multi-layer coverage.

For the **Temkin isotherm** condition number 2 is removed and it is assumed that the energetically most favourable sites are occupied first. The Temkin isotherm corresponds to supposing that the adsorption enthalpy changes linearly with pressure.

The **Freundlich isotherm** removes condition 2 but this isotherm corresponds to a logarithmic change in the adsorption enthalpy with pressure.

Solutions to exercises

E23.1(b) The fast, reversible step suggests the pre-equilibrium approximation:

$$K = \frac{[\mathrm{HAH^+}]}{[\mathrm{HA}][\mathrm{H^+}]} \quad \text{and} \quad [\mathrm{HAH^+}] = K[\mathrm{HA}][\mathrm{H^+}]$$

Thus, the rate of product formation is

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_b[\mathrm{HAH^+}][\mathrm{B}] = \boxed{k_bK[\mathrm{HA}][\mathrm{H^+}][\mathrm{B}]}$$

E23.2(b) Since $v = \dfrac{v_{\max}}{1 + K_M/[\mathrm{S}]_0}$ [23.3a],

$$\begin{aligned} v_{\max} &= (1 + K_M/[\mathrm{S}]_0)v \\ &= (1 + 0.032/0.875) \times (0.205\ \mathrm{mmol\ dm^{-3}\ s^{-1}}) \\ &= \boxed{0.212\ \mathrm{mmol\ dm^{-3}\ s^{-1}}} \end{aligned}$$

E23.3(b)

$$\begin{aligned} k_{\mathrm{cat}} &= v_{\max}/[\mathrm{E}]_0 \ [23.4] \\ &= (0.0224\ \mathrm{mmol\ dm^{-3}\ s^{-1}})/(1.60 \times 10^{-6}\ \mathrm{mmol\ dm^{-3}}) = \boxed{1.40 \times 10^4\ \mathrm{s^{-1}}} \end{aligned}$$

$$\begin{aligned} \eta &= k_{\mathrm{cat}}/K_M \ [23.5] \\ &= (1.40 \times 10^4\ \mathrm{s^{-1}})/(9.0 \times 10^5\ \mathrm{mol\ dm^{-3}}) = \boxed{0.015\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \end{aligned}$$

Diffusion limits the **catalytic efficiency**, η, to a maximum of about 10^8–10^9 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$. Since the catalytic efficiency of this enzyme is much, much smaller than the maximum, the enzyme is not 'catalytically perfect'.

E23.4(b) Eqn 23.7 describes competitive inhibition as the case for which $\alpha = 1 + [\mathrm{I}]/K_I$ and $\alpha' = 1$. Thus,

$$v = \frac{v_{\max}}{1 + \alpha K_M/[\mathrm{S}]_0}$$

By setting the ratio $v([\mathrm{I}] = 0)/v([\mathrm{I}])$ equal to 1/0.25 (4.00) and solving for α, we can subsequently solve for the inhibitor concentration that reduces the catalytic rate by 75%:

$$\frac{v([\mathrm{I}] = 0)}{v([\mathrm{I}])} = \frac{1 + \alpha K_M/[\mathrm{S}]_0}{1 + K_M/[\mathrm{S}]_0} = 4.00$$

$$\begin{aligned} \alpha &= \frac{1.333(1 + K_M/[\mathrm{S}]_0) - 1}{K_M/[\mathrm{S}]_0} \\ &= \frac{4.00(1 + 7.5/1.0) - 1}{7.5/1.0} = 4.40 \end{aligned}$$

$$\begin{aligned} [\mathrm{I}] &= (\alpha - 1)K_I \\ &= 3.40 \times (0.56\ \mathrm{mmol\ dm^{-3}}) = \boxed{1.90\ \mathrm{mmol\ dm^{-3}}} \end{aligned}$$

E23.5(b) The collision frequency, Z_W, of gas molecules with an ideally smooth surface area is given by eqn 23.9:

$$Z_W = \frac{p}{(2\pi MkT/N_A)^{1/2}} \quad [23.9;\ m = M/N_A]$$

$$= \frac{p \times \{(\mathrm{kg\ m^{-1}\ s^{-2}})/\mathrm{Pa}\} \times (10^{-4}\ \mathrm{m^2/cm^2})}{\{2\pi \times (1.381\times10^{-23}\ \mathrm{J\ K^{-1}}) \times (298.15\ \mathrm{K}) \times (\mathrm{kg\ mol^{-1}})/(6.022\times10^{23}\ \mathrm{mol^{-1}})\}^{1/2}\{M/(\mathrm{kg\ mol^{-1}})\}^{1/2}}$$

$$= 4.825\times10^{17}\left(\frac{p/\mathrm{Pa}}{\{M/(\mathrm{kg\ mol^{-1}})\}^{1/2}}\right)\mathrm{cm^{-2}\ s^{-1}} \quad \text{at } 25°\mathrm{C}$$

(a) Nitrogen ($M = 0.02802$ kg mol^{-1})

(i) $p = 10.0$ Pa, $Z_W = \boxed{3.88\times10^{19}\ \mathrm{cm^{-2}\ s^{-1}}}$

(ii) $p = 0.150\ \mu\mathrm{Torr} = 2.00\times10^{-5}$ Pa, $Z_W = \boxed{5.76\times10^{13}\ \mathrm{cm^{-2}\ s^{-1}}}$

(b) Methane ($M = 0.01604$ kg mol^{-1})

(i) $p = 10.0$ Pa, $Z_W = \boxed{3.81\times10^{19}\ \mathrm{cm^{-2}\ s^{-1}}}$

(ii) $p = 0.150\ \mu\mathrm{Torr} = 2.00\times10^{-5}$ Pa, $Z_W = \boxed{7.62\times10^{13}\ \mathrm{cm^{-2}\ s^{-1}}}$

E23.6(b) $A = \pi d^2/4 = \pi(2.0\ \mathrm{mm})^2/4 = 3.14\times10^{-6}\ \mathrm{m^2}$

The collision frequency of the nitrogen gas molecules with surface area A equals Z_WA.

$$Z_WA = \frac{p}{(2\pi MkT/N_A)^{1/2}}A \quad [23.9;\ m = M/N_A]$$

$$p = (Z_WA)\times(2\pi MkT/N_A)^{1/2}/A$$

$$= (5.0\times10^{19}\ \mathrm{s^{-1}})\times\{2\pi(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}})\times(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})$$

$$\times(525\ \mathrm{K})/(6.022\times10^{23}\ \mathrm{mol^{-1}})\}^{1/2}/(3.14\times10^{-6}\ \mathrm{m^2}) = \boxed{733\ \mathrm{Pa}}$$

E23.7(b) The farther apart the atoms responsible for the pattern, the closer the spots appear in the pattern (see Example 23.3). Tripling the horizontal separation between atoms of the unreconstructed face, which has LEED pattern (a), yields a reconstructed surface that gives LEED pattern (b).

(a) (b)

E23.8(b) Let us assume that the carbon monoxide molecules are close packed, as shown in Figure 23.1 as spheres, in the monolayer. Then, one molecule occupies the parallelogram area of $2\sqrt{3}r^2$, where r is the radius of the adsorbed molecule, which is expected to be comparable to the radius of an adsorbed nitrogen molecule. Furthermore, let us assume that the collision cross-section of Table 20.1 ($\sigma = 0.43\ \mathrm{nm^2} = 4\pi r^2$) gives a reasonable estimate of r: $r = (\sigma/4\pi)^{1/2}$. With these assumptions the surface area occupied by one molecule is:

$$A_{\text{molecule}} = 2\sqrt{3}(\sigma/4\pi) = \sqrt{3}\sigma/2\pi = \sqrt{3}(0.43\ \mathrm{nm^2})/2\pi = 0.12\ \mathrm{nm^2}$$

In this model the surface area per gram of the catalyst equals $A_{\text{molecule}}N$, where N is the number of adsorbed molecules. N can be calculated with the 0°C data, a temperature that is so high compared to the boiling point of nitrogen that all molecules are likely to be desorbed from the surface as perfect gas.

$$N = \frac{pV}{kT} = \frac{(1.00\times10^{5}\,\text{Pa})\times(3.75\times10^{-6}\,\text{m}^3)}{(1.381\times10^{-23}\,\text{J K}^{-1})\times(273.15\,\text{K})} = 9.94\times10^{19}$$

$$A_{\text{molecule}}N = (0.12\times10^{-18}\,\text{m}^2)\times(9.94\times10^{19}) = \boxed{12\,\text{m}^2}$$

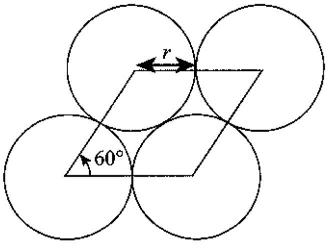


Figure 23.1

E23.9(b) $$\theta = \frac{V}{V_\infty}\,[23.10] = \frac{V}{V_{\text{mon}}} = \frac{Kp}{1+Kp}\,[23.12]$$

This rearranges to [Example 23.4]

$$\frac{p}{V} = \frac{p}{V_{\text{mon}}} + \frac{1}{KV_{\text{mon}}}$$

Hence, $\dfrac{p_2}{V_2} - \dfrac{p_1}{V_1} = \dfrac{p_2}{V_{\text{mon}}} - \dfrac{p_1}{V_{\text{mon}}}$

Solving for V_{mon}:

$$V_{\text{mon}} = \frac{p_2 - p_1}{(p_2/V_2 - p_1/V_1)} = \frac{(108-56.4)\,\text{kPa}}{(108/2.77 - 56.4/1.52)\,\text{kPa cm}^{-3}} = \boxed{27\,\text{cm}^3}$$

E23.10(b) The enthalpy of adsorption is typical of $\boxed{\text{chemisorption}}$ (Table 23.2) for which $\tau_0 \approx 10^{-14}$ s [lSection 23.5(b)] because the adsorbate–substrate bond is stiff. The half-life for remaining on the surface is

$$t_{1/2} = \tau_0 e^{E_{\text{d}}/RT}\,[21.24] \approx (10^{-14}\,\text{s})\times(e^{155\times10^{3}/(8.3145\times500)})\,[E_{\text{d}} \approx -\Delta_{\text{ad}}H] \approx \boxed{200\,\text{s}}$$

E23.11(b) $$\frac{m_1}{m_2} = \frac{\theta_1}{\theta_2} = \frac{p_1}{p_2}\times\frac{1+Kp_2}{1+Kp_1}\,[23.10 \text{ and } 23.12]$$

which solves to

$$K = \frac{(m_1p_2/m_2p_1)-1}{p_2-(m_1p_2/m_2)} = \frac{(m_1/m_2)\times(p_2/p_1)-1}{1-(m_1/m_2)}\times\frac{1}{p_2}$$
$$= \frac{(0.63/0.21)\times(4/36.0)-1}{1-(0.63/0.21)}\times\frac{1}{4.0\,\text{kPa}} = 0.083\,\text{kPa}^{-1}$$

Therefore,

$$\theta_1 = \frac{(0.083\ \text{kPa}^{-1}) \times (36.0\ \text{kPa})}{(1) + (0.083\ \text{kPa}^{-1}) \times (36.0\ \text{kPa})} = \boxed{0.75}\ [23.12] \quad \text{and} \quad \theta_2 = \frac{(0.083) \times (4.0)}{(1) + (0.083) \times (4.0)} = \boxed{0.25}$$

E23.12(b) $\theta = \dfrac{Kp}{1+Kp}$ [23.12], which implies that $p = \left(\dfrac{\theta}{1-\theta}\right)\dfrac{1}{K}$.

(a) $p = (0.20/0.80)/0.548\ \text{kPa}^{-1} = \boxed{0.46\ \text{kPa}}$

(b) $p = (0.75/0.25)/0.548\ \text{kPa}^{-1} = \boxed{5.5\ \text{kPa}}$

E23.13(b) $\theta = \dfrac{Kp}{1+Kp}$ [23.12], which implies that $K = \left(\dfrac{\theta}{1-\theta}\right) \times \left(\dfrac{1}{p}\right)$.

Additionally, $\ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta_{\text{ad}}H}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6.23] $= \dfrac{\Delta_{\text{des}}H}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ $[\Delta_{\text{ad}}H = -\Delta_{\text{des}}H]$.

Since $\theta_2 = \theta_1$, $K_2/K_1 = p_1/p_2$ and

$$\ln\frac{p_1}{p_2} = \frac{\Delta_{\text{des}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \left(\frac{12.2\ \text{kJ mol}^{-1}}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{318\ \text{K}} - \frac{1}{298\ \text{K}}\right) = -0.310$$

which implies that $p_2 = (8.86\ \text{kPa}) \times (e^{0.310}) = \boxed{12.1\ \text{kPa}}$.

E23.14(b) $\theta = \dfrac{Kp}{1+Kp}$ [23.12], which implies that $K = \left(\dfrac{\theta}{1-\theta}\right) \times \left(\dfrac{1}{p}\right)$.

Additionally, $\ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta_{\text{ad}}H}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6.23] or $\Delta_{\text{ad}}H = -R\ln\left(\dfrac{K_2}{K_1}\right) \times \left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)^{-1}$.

Since $\theta_2 = \theta_1$, $K_2/K_1 = p_1/p_2$ and

$$\Delta_{\text{ad}}H = -R\ln\left(\frac{p_1}{p_2}\right) \times \left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}$$

$$= -(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{350\ \text{kPa}}{1.02 \times 10^3\ \text{kPa}}\right) \times \left(\frac{1}{240\ \text{K}} - \frac{1}{180\ \text{K}}\right)^{-1} = \boxed{-6.40\ \text{kJ mol}^{-1}}.$$

E23.15(b) The desorption time for a given volume is proportional to the half-life of the absorbed species and, consequently, the ratio of desorption times at two different temperatures is given by:

$$t(2)/t(1) = t_{1/2}(2)/t_{1/2}(1) = e^{E_d/RT_2}/e^{E_d/RT_1}\ [23.24] = e^{E_d(1/T_2 - 1/T_1)/R}$$

Solving for the activation energy for desorption, E_d, gives:

$$E_d = R\ln\{t(2)/t(1)\}(1/T_2 - 1/T_1)^{-1} = (8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{8.44\ \text{s}}{1856\ \text{s}}\right) \times \left(\frac{1}{1012\ \text{K}} - \frac{1}{873\ \text{K}}\right)^{-1}$$

$$= \boxed{285\ \text{kJ mol}^{-1}}$$

The desorption time, t, for the same volume at temperature T is given by:

$$t = t(1)\mathrm{e}^{E_\mathrm{d}(1/T-1/T_1)/R} = (1856\ \mathrm{s})\exp\left\{(285\times10^3\ \mathrm{J\ mol^{-1}})\times\left(\frac{1}{T}-\frac{1}{873\ \mathrm{K}}\right)/(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\right\}$$

$$= (1856\ \mathrm{s})\exp\left\{(34.3)\times\left(\frac{1}{T/1000\ \mathrm{K}}-\frac{1}{0.873}\right)\right\}$$

(a) At 298 K, $t = \boxed{1.56\times10^{36}\ \mathrm{s}}$.

(b) At 1500 K, $t = \boxed{1.37\times10^{-4}\ \mathrm{s}}$.

E23.16(b) The average time of molecular residence is proportional to the half-life of the absorbed species and, consequently, the ratio of average residence times at two different temperatures is given by:

$$t(2)/t(1) = t_{1/2}(2)/t_{1/2}(1) = \mathrm{e}^{E_\mathrm{d}/RT_2}/\mathrm{e}^{E_\mathrm{d}/RT_1}\ [23.24] = \mathrm{e}^{E_\mathrm{d}(1/T_2-1/T_1)/R}$$

Solving for the activation energy for desorption, E_d, gives:

$$E_\mathrm{d} = R\ln\{t(2)/t(1)\}(1/T_2-1/T_1)^{-1} = R\ln\{0.65\times t(1)/t(1)\}(1/T_2-1/T_1)^{-1} = R\ln\{0.65\}(1/T_2-1/T_1)^{-1}$$

$$= (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times\ln(0.65)\times\left(\frac{1}{1000\ \mathrm{K}}-\frac{1}{600\ \mathrm{K}}\right)^{-1} = \boxed{5.34\ \mathrm{kJ\ mol^{-1}}}$$

E23.17(b) At 298 K: $t_{1/2} = \tau_0\mathrm{e}^{E_\mathrm{d}/RT}\ [23.24] = (0.12\ \mathrm{ps})\times\mathrm{e}^{0.404E_\mathrm{d}/\mathrm{kJ\ mol^{-1}}}$

At 800 K: $t_{1/2} = \tau_0\mathrm{e}^{E_\mathrm{d}/RT}\ [23.24] = (0.12\ \mathrm{ps})\times\mathrm{e}^{0.150E_\mathrm{d}/\mathrm{kJ\ mol^{-1}}}$

(a) $E_\mathrm{d} = 20\ \mathrm{kJ\ mol^{-1}}$

$$t_{1/2}(298\ \mathrm{K}) = (0.12\ \mathrm{ps})\times\mathrm{e}^{0.404\times20} = \boxed{38\bar{8}\ \mathrm{ps}},\ t_{1/2}(800\ \mathrm{K}) = (0.12\ \mathrm{ps})\times\mathrm{e}^{0.150\times20} = \boxed{2.4\ \mathrm{ps}}$$

(b) $E_\mathrm{d} = 200\ \mathrm{kJ\ mol^{-1}}$

$$t_{1/2}(298\ \mathrm{K}) = (0.12\ \mathrm{ps})\times\mathrm{e}^{0.404\times200} = \boxed{1.5\times10^{22}\ \mathrm{s}},\ t_{1/2}(800\ \mathrm{K}) = (0.12\ \mathrm{ps})\times\mathrm{e}^{0.150\times200} = \boxed{1.3\ \mathrm{s}}$$

Solutions to problems

Solutions to numerical problems

P23.2 (a) $$v = \frac{v_\mathrm{max}}{1+K_\mathrm{M}/[S]_0}\ [23.3\mathrm{a}]$$

Taking the inverse and multiplying by $v_\mathrm{max}v$, we find that

$$v_\mathrm{max} = v + K_\mathrm{M}v/[\mathrm{S}]_0$$

Thus, $v = v_\mathrm{max} - K_\mathrm{M}\dfrac{v}{[\mathrm{S}]_0}$ (Eadie–Hofstee plot) or $\boxed{\dfrac{v}{[\mathrm{S}]_0} = \dfrac{v_\mathrm{max}}{K_\mathrm{M}} - \dfrac{v}{K_\mathrm{M}}}$

Alternatively, to see the rationale for the Hanes–Woolf plot of $[\mathrm{S}]_0/v$ against $[\mathrm{S}]_0$, write eqn 23.3a in the form

$$v=\frac{v_{\max}[S]_0}{[S]_0+K_{\mathrm{M}}}\quad[23.3\mathrm{a}]$$

Now divide by $[\mathrm{S}]_0$ and take the inverse to get

$$\boxed{\frac{[S]_0}{v}=\frac{1}{v_{\max}}[S]_0+\frac{K_{\mathrm{M}}}{v_{\max}}}\quad\text{[Hanes–Woolf plot]}$$

(b) The regression slope and intercept of the Eadie–Hofstee data plot of v against $v/[\mathrm{S}]_0$ are $-K_{\mathrm{M}}$ and $v_{\max}$, respectively. Alternatively, the regression slope and intercept of the alternative form of the Eadie–Hofstee data plot of $v/[\mathrm{S}]_0$ against v gives $-1/K_{\mathrm{M}}$ and $v_{\max}/K_{\mathrm{M}}$, respectively; the slope and intercept can be used in the calculation of K_{M} and $v_{\max}$. In contrast, the Hanes–Woolf plot of $[\mathrm{S}]_0/v$ against $[\mathrm{S}]_0$ has a regression slope of $1/v_{\max}$ and an intercept of $K_{\mathrm{M}}/v_{\max}$. Once again the slope and intercept of the latter plot can be used in the calculation of K_{M} and $v_{\max}$.

(c) We draw up the following table, which includes data rows required for both an Eadie–Hofstee plot (v against $v/[\mathrm{S}]_0$, Figure 23.2) and a Hanes–Woolf plot ($[\mathrm{S}]_0/v$ against $[\mathrm{S}]_0$, Figure 23.3). The linear regression fit is displayed in each plot.

[ATP]/(μmol $\mathrm{dm^{-3}}$)	0.60	0.80	1.4	2.0	3.0
v/(μmol $\mathrm{dm^{-3}\,s^{-1}}$)	0.81	0.97	1.30	1.47	1.69
v/[ATP]/$\mathrm{s^{-1}}$	1.35	1.21	0.929	0.735	0.563
[ATP]/v/s	0.741	0.826	1.08	1.36	1.78

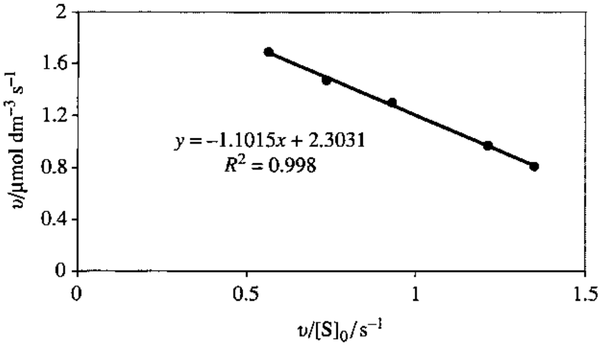


Figure 23.2

Eadie–Hofstee analysis:

$v_{\max} = \mathit{intercept} = \boxed{2.30\ \mu\mathrm{mol\ dm^{-3}\ s^{-1}}}$ and $K_M = -\mathit{slope} = \boxed{1.10\ \mu\mathrm{mol\ dm^{-3}}}$.

Hanes–Woolf analysis:

$v_{\max} = 1/\mathit{slope} = \boxed{2.31\ \mu\mathrm{mol\ dm^{-3}\ s^{-1}}}$ and $K_M = \mathit{intercept} \times v_{\max} = \boxed{1.10\ \mu\mathrm{mol\ dm^{-3}}}$.

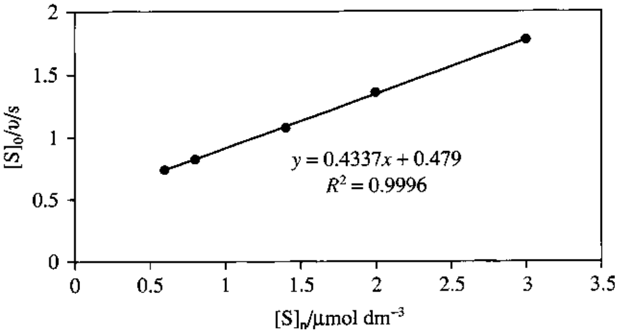


Figure 23.3

P23.4 When using reaction rates v, the Lineweaver–Burk plot without inhibition has the form:

$$\frac{1}{v}=\frac{1}{v_{\max}}+\left(\frac{K_{\mathrm{M}}}{v_{\max}}\right)\frac{1}{[\mathrm{S}]_0}\ [23.3\mathrm{b}]$$

where the intercept and slope are simple functions of $v_{\max}$ and K_{M}. When using reaction rates relative to a specific, non-inhibited rate ($v_{\mathrm{rel}} = v/v_{\mathrm{reference}}$), the Lineweaver–Burk plot without inhibition has the same basic form:

$$\frac{1}{v_{\mathrm{rel}}}=\frac{1}{v_{\max,\mathrm{rel}}}+\left(\frac{K_{\mathrm{M}}}{v_{\max,\mathrm{rel}}}\right)\frac{1}{[\mathrm{S}]_0}$$

The linear regression fit of the non-inhibited Lineweaver–Burk data plot is

$$\frac{1}{v_{\mathrm{rel}}}=0.797+(2.17)\frac{1}{[\mathrm{CBGP}]_0/10^{-2}\,\mathrm{mol\,dm^{-3}}}\qquad R^2=0.980$$

Consequently, $v_{\max,\mathrm{rel}} = 1/\mathit{intercept} = 1/0.797 = 1.25$ and

$K_{\mathrm{M}} = \mathit{slope} \times v_{\max,\mathrm{rel}} = (2.17\times10^{-2}\,\mathrm{mol\,dm^{-3}})\times(1.25) = 2.71\times10^{-2}\,\mathrm{mol\,dm^{-3}}$.

The Lineweaver–Burk plot with inhibition has the basic form:

$$\frac{1}{v_{\mathrm{rel}}}=\frac{\alpha'}{v_{\max,\mathrm{rel}}}+\left(\frac{\alpha K_{\mathrm{M}}}{v_{\max,\mathrm{rel}}}\right)\frac{1}{[\mathrm{S}]_0}$$

The linear regression fit of the Lineweaver–Burk data plot for phenylbutyrate ion inhibition is

$$\frac{1}{v_{\mathrm{rel}}}=1.02+(6.01)\frac{1}{[\mathrm{CBGP}]_0/10^{-2}\,\mathrm{mol\,dm^{-3}}}\qquad R^2=0.972$$

Therefore, $\alpha' = \mathit{intercept}\times v_{\max,\mathrm{rel}} = 1.02\times1.25 = 1.28$ and

$\alpha = \mathit{slope}\times v_{\max,\mathrm{rel}}/K_{\mathrm{M}} = (6.01\times10^{-2}\,\mathrm{mol\,dm^{-3}})\times(1.25)/(2.71\times10^{-2}\,\mathrm{mol\,dm^{-3}}) = 2.77$

Since both $\alpha > 1$ and $\alpha' \sim 1$ (see Section 23.2c), we conclude that $\boxed{\text{phenylbutyrate ion is a competitive inhibitor of carboxypeptidase}}$.

The linear regression fit of the Lineweaver–Burk data plot for benzoate ion inhibition is

$$\frac{1}{v_{\mathrm{rel}}} = 3.75 + (3.01)\frac{1}{[\mathrm{CBGP}]_0/10^{-2}\ \mathrm{mol\ dm^{-3}}} \qquad R^2 = 0.999$$

Therefore, $\alpha' = \mathit{intercept} \times v_{\mathrm{max,rel}} = 3.75 \times 1.25 = 4.69$ and

$$\alpha = \mathit{slope} \times v_{\mathrm{max,rel}}/K_{\mathrm{M}} = (3.01\times10^{-2}\ \mathrm{mol\ dm^{-3}}) \times (1.25)/(2.71\times10^{-2}\ \mathrm{mol\ dm^{-3}}) = 1.39$$

Since both $\alpha \sim 1$ and $\alpha' > 1$, we conclude that $\boxed{\text{benzoate ion is an uncompetitive inhibitor of}}$ $\boxed{\text{carboxypeptidase}}$.

P23.6

$$Z_{\mathrm{W}} = \frac{p}{(2\pi MkT/N_{\mathrm{A}})^{1/2}}\ [23.9;\ m = M/N_{\mathrm{A}}]$$

$$= \frac{p \times \{(\mathrm{kg\ m^{-1}\ s^{-2}})/\mathrm{Pa}\} \times (10^{-4}\ \mathrm{m^2/cm^2})}{\{2\pi \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (300\ \mathrm{K}) \times (0.03200\ \mathrm{kg\ mol^{-1}})/(6.022 \times 10^{23}\ \mathrm{mol^{-1}})\}^{1/2}}$$

$$= 2.69 \times 10^{18} \times (p/\mathrm{Pa})\ \mathrm{cm^{-2}\ s^{-1}} \quad \text{for } \mathrm{O_2} \text{ at } 300\ \mathrm{K}$$

(a) At 100 kPa, $\boxed{Z_{\mathrm{W}} = 2.69 \times 10^{23}\ \mathrm{cm^{-2}\ s^{-1}}}$ (b) at 1.000 Pa, $\boxed{Z_{\mathrm{W}} = 2.69 \times 10^{18}\ \mathrm{cm^{-2}\ s^{-1}}}$

The nearest neighbour in titanium is 291 pm, so the number of atoms per $\mathrm{cm^2}$ is approximately 1.4×10^{15} (the precise value depends on the details of the packing, which is hcp, and the identity of the surface). The number of collisions per exposed atom is therefore $Z_{\mathrm{W}}/1.4 \times 10^{15}\ \mathrm{cm^{-2}}$.

(a) When $p = 100$ kPa, $Z_{\mathrm{atom}} = \boxed{2.0 \times 10^{8}\ \mathrm{s^{-1}}}$ (b) When $p = 1.000$ Pa, $Z_{\mathrm{atom}} = \boxed{2.0 \times 10^{3}\ \mathrm{s^{-1}}}$

P23.8 We follow Example 23.4 of the text, where it is shown that for a Langmuir isotherm

$$\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty}$$

and draw up the following table:

p/Pa	25	129	253	540	1000	1593
p/V/Pa $\mathrm{cm^{-3}}$	595	791	1145	1682	2433	3382

p/V is plotted against p in Figure 23.4. The plot is observed to be linear so we conclude that the data fits the Langmuir isotherm for these low pressures and, therefore, low coverages. The regression slope equals $1/V_\infty$; the regression intercept equals $1/KV_\infty$. Thus,

$$V_\infty = 1/\mathit{slope} = 1/(1.77\ \mathrm{cm^{-3}}) = \boxed{0.565\ \mathrm{cm^3}}$$

and

$$K = 1/(V_\infty \times \mathit{intercept}) = 1/(0.565\ \mathrm{cm^3} \times 629\ \mathrm{Pa\ cm^{-3}}) = \boxed{2.81 \times 10^{-3}\ \mathrm{Pa^{-1}}}$$

COMMENT. It is unlikely that low-pressure data can be used to obtain an accurate value of the volume corresponding to complete coverage. See Problem 23.10 for adsorption data at higher pressures

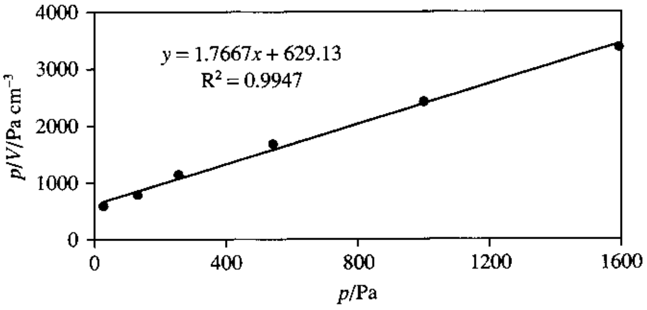


Figure 23.4

P23.10 We assume that the data fit the Langmuir isotherm. To confirm this we plot p/V against p and expect a straight line [Example 23.4]. We draw up the following table and a data plot is shown in Figure 23.5:

p/atm	0.050	0.100	0.150	0.200	0.250
V/cm^3	1.22	1.33	1.31	1.36	1.40
p/V/(10^{-2} atm cm^{-3})	4.10	7.52	11.5	14.7	17.9

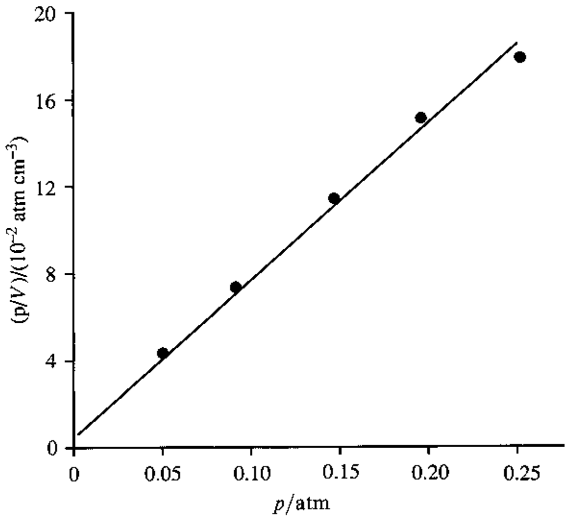


Figure 23.5

The plot fits closely to a straight line with slope 0.694 cm^{-3}. Hence,

$$V_\infty = 1/slope = \boxed{1.44\ \text{cm}^3} = 1.44 \times 10^{-3}\ \text{dm}^3 \approx V_{\text{mon}}$$

The number of H_2 molecules corresponding to this volume is

$$N_{H_2} = \frac{pVN_A}{RT} = \frac{(1.00\ \text{atm}) \times (1.44 \times 10^{-3}\ \text{dm}^3) \times (6.022 \times 10^{23}\ \text{mol}^{-1})}{(0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (273\ \text{K})} = 3.87 \times 10^{19}$$

The area occupied is the number of molecules times the area per molecule. The area per molecule can be estimated from the density of the liquid.

$$A=\pi\left(\frac{3V}{4\pi}\right)^{2/3}=\pi\left(\frac{3M}{4\pi\rho N_A}\right)^{2/3}\left[V=\text{volume of molecule}=\frac{M}{\rho N_A}\right]$$

$$=\pi\left(\frac{3\times(2.02\ \text{g mol}^{-1})}{4\pi\times(0.708\ \text{g cm}^{-3})\times(6.022\times10^{23}\ \text{mol}^{-1})}\right)^{2/3}$$

$$=3.41\times10^{-16}\ \text{cm}^2$$

Area occupied $=(3.87\times10^{19})\times(3.41\times10^{-16}\ \text{cm}^2)=1.3\times10^4\ \text{cm}^2=\boxed{1.3\ \text{m}^2}$

COMMENT. The value for V_∞ calculated here may be compared to the value obtained in Problem 23.8. The agreement is not good and illustrates the point that these kinds of calculations provide only rough value surface areas.

P23.12 We assume that the Langmuir isotherm applies.

$$\theta=\frac{Kp}{1+Kp}\ [23.12]\quad\text{and}\quad 1-\theta=\frac{1}{1+Kp}$$

For a strongly adsorbed species, $Kp \gg 1$ and $1-\theta=1/Kp$. Since the reaction rate is proportional to the pressure of ammonia and the fraction of sites left uncovered by the strongly adsorbed hydrogen product, we can write

$$\frac{\mathrm{d}p_{NH_3}}{\mathrm{d}t}=-k_c p_{NH_3}(1-\theta)\approx\boxed{-\frac{k_c p_{NH_3}}{Kp_{H_2}}}$$

To solve the rate law, we write

$$p_{H_2}=\tfrac{3}{2}\{p_{0,NH_3}-p_{NH_3}\}\ [NH_3\rightarrow\tfrac{1}{2}N_2+\tfrac{3}{2}H_2]$$

from which it follows that, with $p=p_{NH_3}$

$$\frac{-\mathrm{d}p}{\mathrm{d}t}=\frac{kp}{p_0-p},\ k=\frac{2k_c}{3K}$$

This equation integrates as follows

$$\int_{p_0}^{p}\left(1-\frac{p_0}{p}\right)\mathrm{d}p=k\int_0^t\mathrm{d}t$$

$$\text{or}\ \boxed{\frac{p-p_0}{t}=k+\frac{p_0}{t}\ln\frac{p}{p_0}}$$

We write $F'=(p_0/t)\ln(p/p_0)$, $G=(p-p_0)/t$

and obtain $G=k+F'=k+p_0F$.

Hence, a plot of G against F' should give a straight line with intercept k at $F'=0$. Alternatively, the difference $G-F'$ should be a constant, k. We draw up the following table:

t/s	0	30	60	100	160	200	250
p/kPa	13.3	11.7	11.2	10.7	10.3	9.9	9.6
$G/(\text{kPa s}^{-1})$		−0.053	−0.035	−0.026	−0.0188	−0.017	−0.015
$F'/(\text{kPa s}^{-1})$		−0.0568	−0.381	−0.0289	−0.0213	−0.0196	−0.0173
$(G-F')/(\text{kPa s}^{-1})$		0.00349	0.00309	0.00293	0.00250	0.00263	0.00254

Thus, the data fit the rate law, and we find $\boxed{k = 0.0029\ \text{kPa s}^{-1}}$ with a standard deviation of 0.0004 kPa s^{-1}.

P23.14 Application of the van't Hoff equation [6.21] to adsorption equilibria yields

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_{\text{ad}}H^{\circ}}{RT^2}\ [23.15] \quad \text{or} \quad \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{-\Delta_{\text{ad}}H^{\circ}}{R}$$

Hence, since $\Delta_{\text{ad}}H^{\circ}$ is expected to have no temperature dependence, a plot of ln K against $1/T$ should be a straight line with slope $-\Delta_{\text{ad}}H^{\circ}/R$. The transformed data and plot (Figure 23.6) follow.

T/K	283	298	308	318
10^{-11} K	2.642	2.078	1.286	1.085
1000 K/T	3.53	3.36	3.25	3.14
ln K	26.30	26.06	25.58	25.41

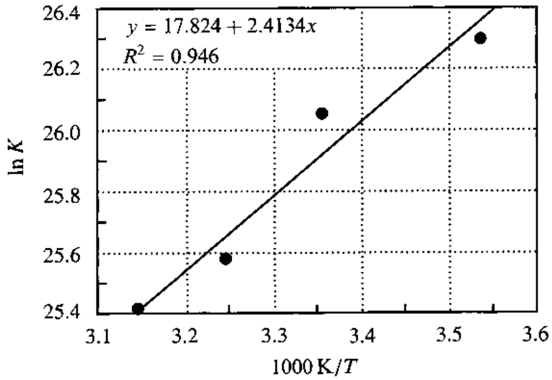


Figure 23.6

$$\Delta_{\text{ad}}H^{\circ} = -R \times slope = -(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) \times (2.41 \times 10^3\ \text{K})$$
$$= -20.0 \times 10^3\ \text{J mol}^{-1} = \boxed{-20.0\ \text{kJ mol}^{-1}}$$

The Gibbs energy for absorption is

$$\Delta_{\text{ad}}G^{\circ} = \Delta_{\text{ad}}H^{\circ} - T\Delta_{\text{ad}}S^{\circ} = -20.0\ \text{kJ mol}^{-1} - (298\ \text{K}) \times (0.146\ \text{kJ mol}^{-1}\ \text{K}^{-1})$$
$$= \boxed{-63.5\ \text{kJ mol}^{-1}}.$$

P23.16 We must adapt the Langmuir gas adsorption isotherm, $\frac{p}{V}=\frac{p}{V_\infty}+\frac{1}{KV_\infty}$ [Example 23.4], so that it describes adsorption from solution. This can be done with the transforms: $p \rightarrow$ concentration, c and $V \rightarrow$ amount adsorbed per gram adsorbent, s. This gives

Langmuir isotherm and regression analysis:

$$\frac{c}{s}=\frac{c}{s_\infty}+\frac{1}{Ks_\infty} \text{ [Langmuir solution isotherm]}$$

This says that a plot of c/s against c should be linear and we find that the linear regression fit of the data gives

$$\textit{slope}=\frac{1}{s_\infty}=0.163\text{ g mmol}^{-1}\text{, standard deviation}=0.017\text{ g mmol}^{-1}$$

$$\textit{intercept}=\frac{1}{Ks_\infty}=35.6\,(\text{mmol dm}^{-3})\times(\text{g mmol}^{-1})\text{, standard deviation}$$
$$=5.9\,(\text{mmol dm}^{-3})\times(\text{g mmol}^{-1})$$

$$\boxed{R(\text{Langmuir})=0.973}$$

$$K=\frac{\textit{slope}}{\textit{intercept}}=\frac{0.163\text{ g mmol}^{-1}}{35.6\,(\text{mmol dm}^{-3})\times(\text{g mmol}^{-1})}=0.0046\text{ dm}^3\text{ mmol}^{-1}$$

Similarly, the Freundlich solution isotherm [23.20] and regression analysis of the data is:

$$s=c_1(c/\text{mmol dm}^{-3})^{1/c_2}\quad\text{or}\quad\ln(s/\text{mmol g}^{-1})=\ln(c_1/\text{mmol g}^{-1})+\tfrac{1}{c_2}\ln(c/\text{mmol dm}^{-3})$$

This says that a plot of $\ln(s/\text{mmol g}^{-1})$ against $\ln(c/\text{mmol dm}^{-3})$ should be linear and we find that the linear regression fit of the data gives

$$c_1=e^{\textit{intercept}}\text{ mmol dm}^{-3}=0.139\text{ mmol dm}^{-3}\text{, standard deviation}=0.012\text{ mmol dm}^{-3}$$

$$\textit{slope}=\frac{1}{c_2}=0.539,\quad\text{standard deviation}=0.003$$

$$\boxed{R(\text{Freundlich})=0.999\,94}$$

The Temkin solution isotherm [23.19] and regression analysis gives:

$$s=c_1\ln(c_2c/\text{mmol dm}^{-3})$$

$$c_1=1.08\text{ mmol dm}^{-3},\quad\text{standard deviation}=0.14\text{ mmol dm}^{-3}$$

$$c_2=0.074,\quad\text{standard deviation}=0.023$$

$$\boxed{R(\text{Temkin})=0.9590}$$

The correlation coefficients and standard deviations indicate that the $\boxed{\text{Freundlich isotherm}}$ provides the best fit of the data.

Solutions to theoretical problems

P23.18 The description of the progress of infectious diseases can be represented by the mechanism

$$S \rightarrow I \rightarrow R$$

Only the $\boxed{\text{first step is autocatalytic}}$, as indicated in the first rate expression. If the three rate equations are added

$$\frac{dS}{dt} + \frac{dI}{dt} + \frac{dR}{dt} = 0$$

and hence there is no change with time of the total population, that is

$$S(t) + I(t) + R(t) = N$$

Whether the infection spreads or dies out is determined by

$$\frac{dI}{dt} = rSI - aI$$

At $t = 0$, $I = I(0) = I_0$. Since the process is autocatalytic, $I(0) \neq 0$.

$$\left(\frac{dI}{dt}\right)_{t=0} = (rS_0 - a)I_0$$

If $a > rS_0$, $\left(\frac{dI}{dt}\right)_{t=0} < 0$, and the infection dies out. If $a < rS$, $\left(\frac{dI}{dt}\right)_{t=0} > 0$ and the infection spreads (an epidemic). Thus,

$$\boxed{\frac{a}{r} < S_0} \text{ [infection spreads]} \quad \text{and} \quad \boxed{\frac{a}{r} > S_0} \text{ [infection dies out]}$$

P20.20 Assume that the steady-state approximation is appropriate for both intermediates ([ES] and [ES′]).

For [ES]:

$$\frac{d[ES]}{dt} = k_a[E][S] - k_a'[ES] - k_b[ES] = 0 \quad \text{and} \quad [ES] = \left(\frac{k_a}{k_a' + k_b}\right)[E][S]$$

For [ES′]:

$$\frac{d[ES']}{dt} = k_b[ES] - k_c[ES'] = 0 \quad \text{and} \quad [ES'] = \left(\frac{k_b}{k_c}\right)[ES]$$

We now have two equations in the three unknowns [E], [ES], and [ES′]. A third is provided by the mass-balance expression $[E]_0 = [E] + [ES] + [ES']$. These three equations may be solved to give expressions for each of the three unknowns in terms of the rate constants, $[E]_0$, and [S]. (For practical purposes the free substrate concentration is replaced by $[S]_0$ because the substrate is typically in large excess relative to the enzyme.) The expression found for [ES′] is

$$[ES'] = \frac{v_{\max}/k_c}{1 + K_M/[S]_0}, \quad \text{where} \quad v_{\max} = \left(\frac{k_b k_c}{k_b + k_c}\right)[E]_0 \quad \text{and} \quad K_M = \frac{k_c(k_a' + k_b)}{k_a(k_b + k_c)}$$

Substitution into the rate expression for product formation yields the desired equation:

$$v = k_c[\mathrm{ES}'] = \frac{v_{\max}}{1 + K_M/[\mathrm{S}]_0}$$

P23.22 Refer to Figure 23.7.

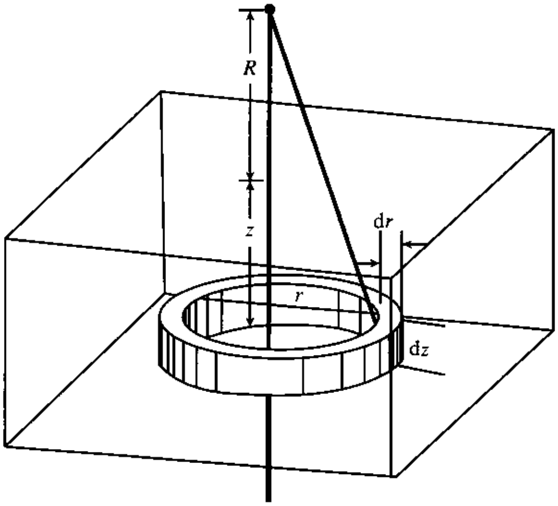


Figure 23.7

Let the number density of atoms in the solid be $\mathcal{N}$. Then, the number in the annulus between r and $r + \mathrm{d}r$ and thickness $\mathrm{d}z$ at a depth z below the surface is $2\pi\mathcal{N}r\,\mathrm{d}r\,\mathrm{d}z$. The interaction energy of these atoms and the single adsorbate atom at a height R above the surface is

$$\mathrm{d}U = \frac{-2\pi\mathcal{N}r\,\mathrm{d}r\,\mathrm{d}z\,C_6}{\{(R+z)^2 + r^2\}^3}$$

if the individual atoms interact as $-C_6/d^6$ with $d^2 = (R+z)^2 + r^2$. The total interaction energy of the atom with the semi-infinite slab of uniform density is therefore

$$U = -2\pi\mathcal{N}C_6\int_0^\infty \mathrm{d}r\int_0^\infty \mathrm{d}z\,\frac{r}{\{(R+z)^2 + r^2\}^3}.$$

We then use

$$\int_0^\infty \frac{r\,\mathrm{d}r}{(a^2+r^2)^3} = \frac{1}{2}\int_0^\infty \frac{\mathrm{d}(r^2)}{(a^2+r^2)^3} = \frac{1}{2}\int_0^\infty \frac{\mathrm{d}x}{(a^2+x)^3} = \frac{1}{4a^4}$$

and obtain

$$U = -\frac{1}{2}\pi\mathcal{N}C_6\int_0^\infty \frac{\mathrm{d}z}{(R+z)^4} = \boxed{-\frac{\pi\mathcal{N}C_6}{6R^3}}$$

This result confirms that $U \propto 1/R^3$. (A shorter procedure is to use a dimensional argument, but we need the explicit expression in the following.) When

$$V = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] = \frac{C_{12}}{R^{12}} - \frac{C_6}{R^6}$$

we also need the contribution from C_{12}

$$U' = 2\pi\mathcal{N}C_{12}\int_0^\infty \mathrm{d}r\int_0^\infty \mathrm{d}z\frac{r}{\{(R+z)^2+r^2\}^6} = 2\pi\mathcal{N}C_{12}\times\frac{1}{10}\int_0^\infty\frac{\mathrm{d}z}{(R+z)^{10}} = \frac{2\pi\mathcal{N}C_{12}}{90R^9}$$

and therefore the total interaction energy is

$$U = \frac{2\pi\mathcal{N}C_{12}}{90R^9} - \frac{\pi\mathcal{N}C_6}{6R^3}$$

We can express this result in terms of ε and σ by noting that $C_{12} = 4\varepsilon\sigma^{12}$ and $C_6 = 4\varepsilon\sigma^6$, for then

$$U = 8\pi\varepsilon\sigma^3\mathcal{N}\left[\frac{1}{90}\left(\frac{\sigma}{R}\right)^9 - \frac{1}{12}\left(\frac{\sigma}{R}\right)^3\right]$$

For the position of equilibrium, we look for the value of R for which $\mathrm{d}U/\mathrm{d}R = 0$:

$$\frac{\mathrm{d}U}{\mathrm{d}R} = 8\pi\varepsilon\sigma^3\mathcal{N}\left[-\frac{1}{10}\left(\frac{\sigma^9}{R^{10}}\right) + \frac{1}{4}\left(\frac{\sigma^3}{R^4}\right)\right] = 0$$

Therefore, $\sigma^9/10R^{10} = \sigma^3/4R^4$, which implies that $R = (\tfrac{2}{5})^{1/6}\sigma = \boxed{0.858\sigma}$.

For $\sigma = 342$ pm, $\boxed{R \approx 294 \text{ pm}}$.

Solutions to applications: chemical engineering and environmental science

P23.24 Equilibrium constants vary with temperature according to the van't Hoff equation [6.23 when $\Delta_{\mathrm{ads}}H^{\ominus}$ varies only slightly with temperature], which can be written in the form

$$K_2/K_1 = \mathrm{e}^{-\frac{\Delta_{\mathrm{ads}}H^{\ominus}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}[6.23] = \mathrm{e}^{\frac{-160\times10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{773\,\mathrm{K}}-\frac{1}{673\,\mathrm{K}}\right)} = \boxed{0.0247}$$

As measured by the equilibrium constant of absorption, NO is less strongly absorbed by a factor of 0.0247 at 500°C than at 400°C.

P23.26 (a) $q_{\mathrm{water}} = k(\mathrm{RH})^{1/n}$

With a power law regression analysis we find

$\boxed{k = 0.2289}$, standard deviation = 0.0068

$1/n = 1.6182$, standard deviation = 0.0093; $\boxed{n = 0.6180}$

$R = 0.999508$

A linear regression analysis may be performed by transforming the equation to the following form by taking the logarithm of the Freundlich-type equation.

$$\ln q_{\text{water}} = \ln k + \frac{1}{n}\ln(\text{RH})$$

$$\ln k = -1.4746,\ \text{standard deviation} = 0.0068;\ \boxed{k = 0.2289}$$

$$\frac{1}{n} = 1.6183,\ \text{standard deviation} = 0.0093;\ \boxed{n = 0.6180}$$

$$R = 0.999508$$

The two methods give exactly the same result because the software package for performing the power law regression performs the transformation to linear form for you. Both methods are actually performing a linear regression. The correlation coefficient indicates that 99.95% of the data variation is explained with the Freundlich-type isotherm. The Freundlich-fit hypothesis looks very good.

(b) The Langmuir-isotherm model describes adsorption sites that are independent and equivalent. This assumption seems to be valid for the VOC case in which molecules interact very weakly. However, water molecules interact much more strongly through forces such as hydrogen bonding and multilayers may readily form at the lower temperatures. The intermolecular forces of water apparently cause adsorption sites to become non-equivalent and dependent. In this particular case the Freundlich-type isotherm becomes the better description.

(c) $r_{\text{VOC}} = 1 - q_{\text{water}}$, where $r_{\text{VOC}} \equiv q_{\text{VOC}}/q_{\text{VOC,RH=0}}$

$$r_{\text{VOC}} = 1 - k(\text{RH})^{1/n}$$

$$1 - r_{\text{VOC}} = k(\text{RH})^{1/n}$$

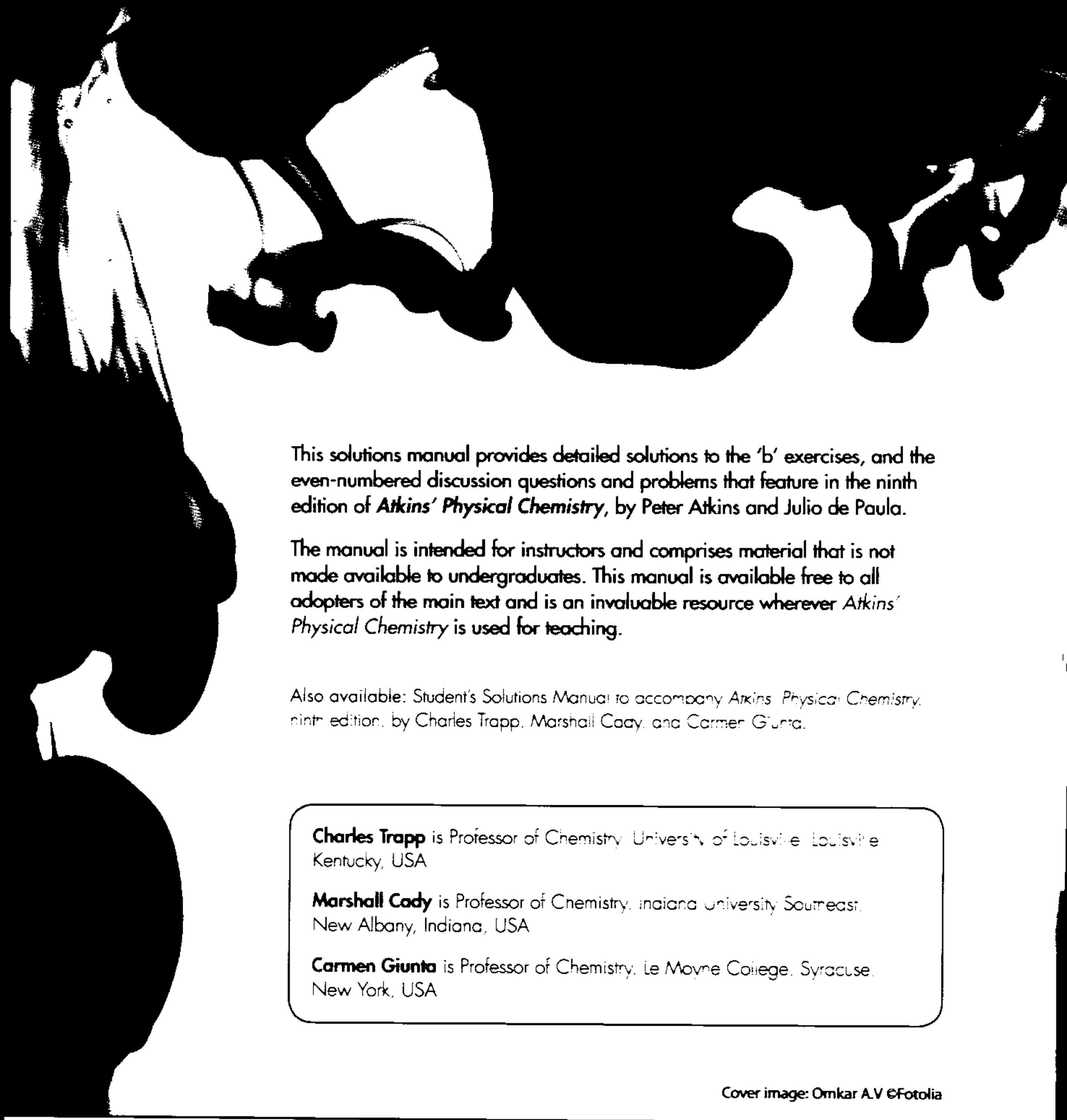
To determine the goodness-of-fit values for k and n, we perform a power-law regression fit of $1 - r_{\text{VOC}}$ against RH. Results are:

$$\boxed{k = 0.5227},\ \text{standard deviation} = 0.0719$$

$$\frac{1}{n} = 1.3749,\ \text{standard deviation} = 0.0601;\ \boxed{n = 0.7273}$$

$$R = 0.99620$$

Since 99.62% of the variation is explained by the regression, we conclude that the hypothesis that $r_{\text{VOC}} = 1 - q_{\text{water}}$ may be very useful. The values of R and n differ significantly from those of part (a). It may be that water is adsorbing to some portions of the surface and VOC to others.



This solutions manual provides detailed solutions to the 'b' exercises, and the even-numbered discussion questions and problems that feature in the ninth edition of ***Atkins' Physical Chemistry***, by Peter Atkins and Julio de Paula.

The manual is intended for instructors and comprises material that is not made available to undergraduates. This manual is available free to all adopters of the main text and is an invaluable resource wherever *Atkins' Physical Chemistry* is used for teaching.

Also available: Student's Solutions Manual to accompany *Atkins' Physical Chemistry*, ninth edition, by Charles Trapp, Marshall Cady, and Carmen Giunta.

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